

PATENT SPECIFICATION

(11) 1 299 080

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NO DRAWINGS

- (21) Application No. 51623/69 (22) Filed 21 Oct. 1969
 (31) Convention Application No. 777 884 (32) Filed 21 Nov. 1968 in
 (33) United States of America (US)
 (45) Complete Specification published 6 Dec. 1972
 (51) International Classification C09B 29/00, 31/00, 33/00, 35/00 // C07C 93/14, 87/68
 (52) Index at acceptance

C4P 1A1B2 1A2B2A 1A2B2B 1A3 1A4B 1D4 1F5 2G2A
 2G2B 2G2C10 2G2C11 2G2C3 2G2C7 2G2C9
 2G3 2H10 2H11 2H12 2H16 2H3 2H5 2H9 3X
 9A3C1 9A4B D1L
 C2C 220 227 22Y 290 29X 29Y 30Y 321 32Y 332 342
 34Y 364 36Y 450 453 45Y 57Y 591 592 593 597
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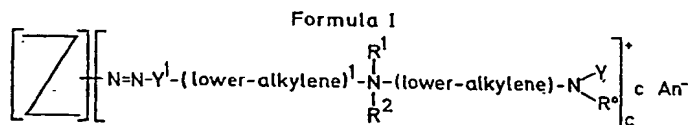


(54) WATER-SOLUBLE QUATERNARY AMMONIUM SALTS OF BASIC AZO DYES

(71) We, STERLING DRUG INC., a Corporation organized under the laws of the State of Delaware, United States of America, of 90 Park Avenue, New York, State of New York, United States of America, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

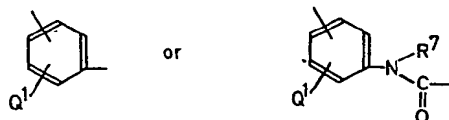
This invention relates to cationic dyestuffs. More particularly, the present invention relates to novel water-soluble quaternary ammonium dyestuffs useful in the dyeing art, particularly for coloring natural fibres, synthetic fiber-forming material and cellulosic materials such as threads, sheets, fibers, filaments and textile fabrics, as well as in the manufacture of paper, varnishes, inks, coatings, and plastics.

The invention deals with novel water-soluble quaternary ammonium azo dyestuffs having the formula



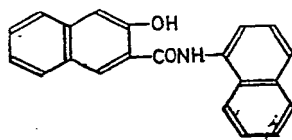
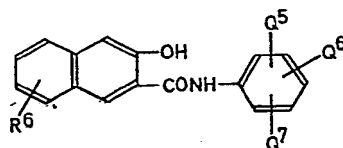
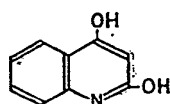
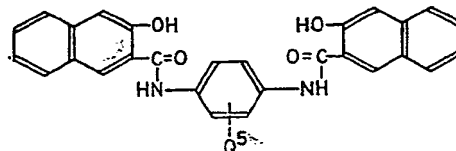
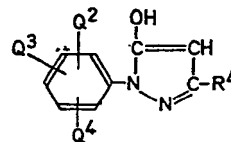
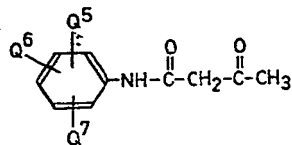
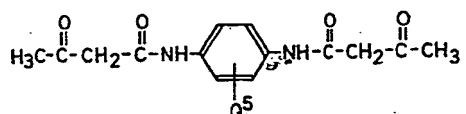
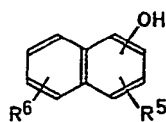
wherein c is one or two; R⁰ is hydrogen, lower-alkyl or hydroxy-lower-alkyl; R¹ is lower-alkyl, lower-alkenyl or hydroxy-lower-alkyl; R² is lower-alkyl, lower-alkenyl, hydroxy-lower-alkyl or -(lower-alkylene)-NR⁰Y or R¹ and R² together with the nitrogen atom to which they are commonly attached, are pyrrolidine, piperidine or

4-lower-alkanoyl-piperazine; Y is hydrogen or $\text{—}\overset{\text{O}}{\parallel}\text{C—R}$ wherein R is hydrogen, lower-alkyl, lower-alkenyl, phenyl or phenyl-lower-alkyl; An is an anion; Y¹ is a divalent moiety of the formula

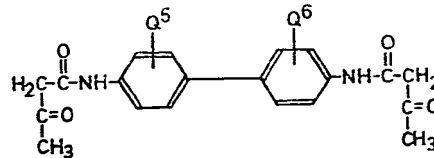


in which Q¹ is hydrogen, lower-alkyl, lower-alkoxy or halogen and R⁷ is hydrogen or

lower-alkyl; and Z is a radical derived from the group of coupling components consisting of

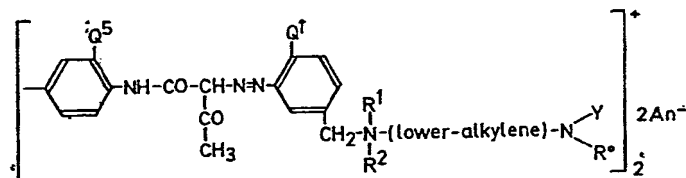


and

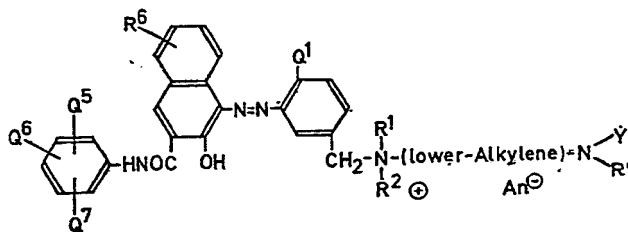


in which Q^2 , Q^3 and Q^4 are each hydrogen, lower-alkyl, lower-alkoxy, hydroxy, nitro, amino, alkoxy, carbonyl, carboxamido, sulphonyl or halogen; Q^5 , Q^6 and Q^7 are each hydrogen, lower alkyl, lower-alkoxy or halogen; R^4 is lower-alkyl, lower-alkoxy, carboxamido or alkoxycarbonyl; R^5 is hydrogen, lower-alkyl, halogen, benzoxazol-2-yl, or benzimidazol-2-yl; and R^6 is hydrogen, lower-alkyl or halogen.

In a preferred dyestuff of Formula 1, c is two, (lower alkylene)¹ is methylene and the dyestuff has the formula:—

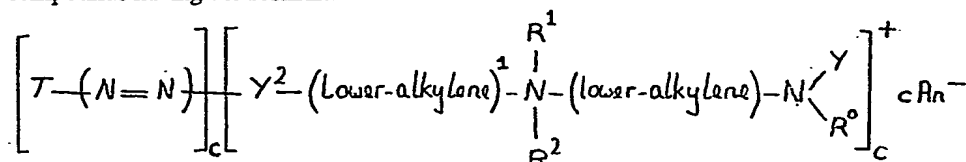


In which Q^1 , Q^5 , R^0 , R^1 , R^2 , Y and An are as defined hereinabove. In another preferred dyestuff of Formula I, c is one, (lower-alkylene)¹ is methylene and the dyestuff has the formula:—



in which Q¹, Q⁵, Q⁶, Q⁷, R⁰, R¹, R², R⁶, Y and An are as defined hereinabove.

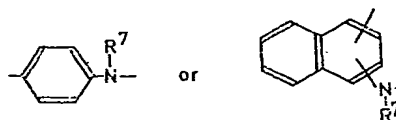
The invention also deals in the novel water-soluble quaternary ammonium azo compounds having the formula



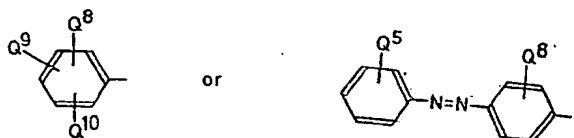
Formula II

wherein c is one or two; R⁰ is hydrogen, lower-alkyl or hydroxy-lower-alkyl; R¹ is lower-alkyl, lower-alkenyl or hydroxy-lower-alkyl; R² is lower-alkyl, lower-alkenyl, hydroxy-lower-alkyl or -(lower-alkylene)-NR⁰Y or R¹ and R² together with the nitrogen atom to which they are commonly attached are pyrrolidine, piperidine or

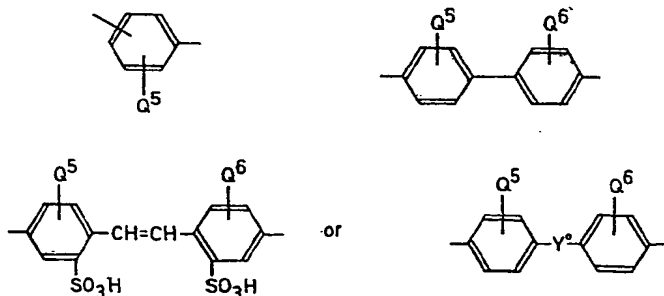
4-lower-alkanoyl-piperazine; Y is hydrogen or $-\overset{\text{O}}{\parallel}-R$ wherein R is hydrogen, lower-alkyl, lower-alkenyl, phenyl or phenyl-lower-alkyl; An is an anion; Y² is a divalent moiety of the formula.



in which the free valence attached to the ring system is bonded to the azo group, and R⁷ is hydrogen or lower-alkyl; and T is either a monovalent residue selected from the group consisting of



when c is one
or a divalent residue which is



when c is two

in which Q⁵ and Q⁶ are each hydrogen, lower-alkyl, lower-alkoxy or halogen, Q⁸ and Q¹⁰ are each hydrogen, lower-alkyl, nitro or halogen, Q⁹ is hydrogen, lower-alkyl, acetamido, nitro or halogen and Y⁰ is azo, methylene, oxo, thio, sulfonyl or ureylene.

As used throughout, the term "lower-alkyl" is a saturated straight- or branched-chain radical of from one to six carbon atoms. Lower-alkyl radicals are represented by, for example, methyl, ethyl, propyl, isopropyl, butyl, *tert.*-butyl, isobutyl, amyl, isoamyl, and hexyl.

As used herein, the term "An" represents Anion. By Anion is meant any monovalent ion derived from an organic or inorganic acid, H Anion, by the removal of an acidic hydrogen ion. Exemplary anions are, halide, hydroxy, alkanoate, nitrate, phosphate, alkylsulfonate and arylsulfonate. Other monovalent anions are found in the literature for example, Hackh's Chemical Dictionary, 4th Edition (1969), at pages 12-14, and Chemical Abstracts, vol. 56, Nomenclature, at pages 72n-80n, both incorporated herein by specific reference thereto. As is known, one anion can be

changed to another anion by use of conventional ion exchange methods. The halides, i.e., chloride, bromide, fluoride and iodide and in particular chloride and bromide are particularly preferred as the anion for the dyestuffs of this invention because of the generally ready availability of the quaternizing agents containing them.

As used throughout, the term "lower-alkenyl" is a straight- or branched-chain radical of from two to six carbon atoms containing at least one carbon-to-carbon double bond. Lower-alkenyl radicals are represented by, for example, vinyl, allyl, methallyl, 2-butenyl, 2,4-pentadienyl, and 3-hexenyl.

As used throughout, the term "(lower-alkylene)" means a divalent, saturated straight- or branched-chain radical of from two to six carbon atoms having valence bonds attached to different carbon atoms. Thus, radicals represented by the term "(lower-alkylene)" are, for example, $-\text{CH}_2\text{CH}_2-$, $-\text{CH}_2-\text{CH}_2-\text{CH}_2-$, $-(\text{CH}_2)_4-$, $-(\text{CH}_2)_5-$, $-(\text{CH}_2)_6-$, $-\text{CH}(\text{CH}_3)\text{CH}_2-$, $-\text{CH}_2-\text{CH}_2-\text{CH}(\text{CH}_3)-\text{CH}_2-$, $-\text{CH}_2-\text{CH}_2-\text{CH}(\text{C}_2\text{H}_5)-\text{CH}_2-$.

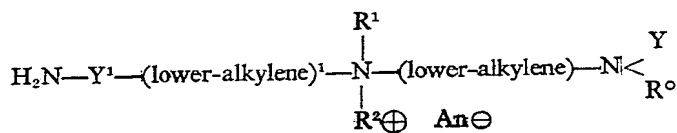
As used throughout, the term "(lower-alkylene)"¹ means methylene or a divalent, saturated straight- or branched-chain radical of from two to six carbon atoms wherein the valence bonds of the two to six carbon atom-containing radical are attached to different carbon atoms. Thus, radicals represented by the term "(lower-alkylene)"¹ have from one to six carbon atoms and are, for example, $-\text{CH}_2-$, $-\text{CH}_2-\text{CH}_2-$, $-\text{CH}_2-\text{CH}_2-\text{CH}_2-$, $-(\text{CH}_2)_4-$, $-(\text{CH}_2)_5-$, $-(\text{CH}_2)_6-$, $-\text{CH}(\text{CH}_3)\text{CH}_2-$, $-\text{CH}_2-\text{CH}_2-\text{CH}(\text{CH}_3)-\text{CH}_2-$, and $-\text{CH}_2-\text{CH}_2-\text{CH}(\text{C}_2\text{H}_5)-\text{CH}_2-$.

The benzene ring of phenyl can bear substituents of the kind commonly employed in the azo-dyestuff art. The presence of such substituents does not ordinarily affect adversely the properties of the resulting dyestuffs, and such substituted phenyl radicals are the full equivalents of the unsubstituted phenyl radicals.

As used throughout, the term "carboxylic-acyl" is a radical derived by the removal of the hydroxy radical from a carboxylic acid. The carboxylic-acyl groups,

$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{R} \end{array}$ (shown alternatively herein as $-\text{COR}$) are represented by lower-alkanoyl, lower-alkenoyl, benzoyl, which may be substituted on the benzene ring thereof without deleterious effects and phenyl-lower alkanoyl. Examples of carboxylic-acyl groups include, for example, formyl, acetyl, propionyl, isobutyryl, acrylyl, methacrylyl, benzoyl, *p*-toluoyl, *p*-nitrobenzoyl, *o*-chlorobenzoyl, phthaloyl phenylacetyl, and *p*-methoxyphenylacetyl.

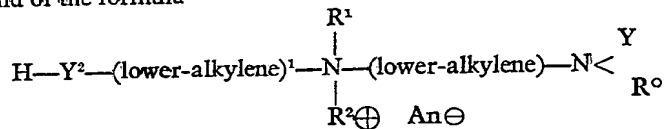
The water-soluble quaternary ammonium azo dyestuffs of Formula I can be prepared by a process which comprises diazotizing an amine of the formula



Formula III

wherein An, R⁰, R¹, R², Y and Y¹ are as defined above in relation to Formula I, and coupling approximately c molecular proportion of the diazonium salt with one molecular proportion of a coupling component, Z, which has the same meanings given hereinabove in relation to Formula I, and, if desired, hydrolyzing with dilute aqueous mineral acid a compound obtained wherein Y is lower-alkanoyl, lower-alkenoyl, benzoyl or phenyl-lower-alkanoyl to obtain the corresponding compound wherein Y is hydrogen.

The water-soluble quaternary ammonium azo dyestuffs of Formula II can be prepared by a process which comprises coupling approximately c molecular proportions of a compound of the formula



Formula IV

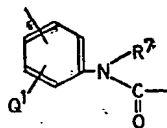
wherein An, R^o, R¹, R², Y and Y² are as defined above in relation to Formula II, with one molecular proportion of the diazonium salt obtained by diazotization of an amine having the formula T-(NH₂)_c wherein c and T have the same meanings given hereinbefore in relation to Formula II, and if desired, hydrolyzing with dilute aqueous mineral acid a compound obtained wherein Y is lower-alkanoyl, lower alkenoyl, benzoyl or phenyl-lower-alkanoyl to obtain the corresponding compound wherein Y is hydrogen.

In the preparation of the dyestuffs of Formula I the ratio of the quantity of diazonium compound to coupling component is, of course, dependent on the number of coupling sites available in the coupling component. Thus when a single coupling site is present, for example in a 3-phenyl-5-pyrazolone, there is employed approximately one molecular proportion of the diazonium compound and when two coupling sites are available as, for example, in 4,4'-bi-*o*-acetoacetotoluidide (Naphthol AS-G), there are employed approximately two molecular proportions of the diazonium compound. In the preparation of those compounds of Formula I wherein two azo linkages are present, there is employed approximately one-half molecular proportion of the tetrazonium compound for reaction with approximately one molecular proportion of the quaternary ammonium coupling component. Since the reaction temperature has some effect on the shade of the resulting water-soluble quaternary ammonium dyestuffs, it is ordinarily desirable to maintain adequate control of the temperature of the reaction mixture in some predetermined manner. It is generally satisfactory to stir the reactants together at a temperature in the approximate range 0—35°C. to effect only an incomplete coupling reaction, and then heat the mixture at a higher temperature, for instance in the approximate range 40—60°C., preferably at 50—55°C., to complete the coupling reaction and develop the dyestuff. The reaction is begun in an alkaline aqueous medium but the pH of the reaction mixture drops during the process to a final value of about 5.0.

The water-soluble quaternary ammonium azo dyestuffs of Formula I and of Formula II wherein Y is hydrogen can also be prepared by hydrolyzing a compound of Formula I or of Formula II wherein Y is —COR in which R is as defined above. The removal of the carboxylic acyl groups is conveniently accomplished through hydrolysis by heating the acylamino dyestuffs in admixture with dilute aqueous acid. Although the hydrolysis is effectively accomplished by the use of any of the common dilute mineral acids as well as by aqueous strong organic acids as previously enumerated, we here also prefer to hydrolyze the acylamine groups with a dilute aqueous acid whose anion is the same as the quaternary anion in order to prevent introduction of extraneous anion contaminants. Moreover, the carboxylic-acyl-amides of Formula I and of Formula II may also be hydrolyzed by aqueous alkali, but of course, with concomitant introduction of the hydroxide ion as an anion contaminant.

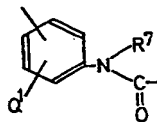
Alternatively, the dyestuffs of Formula I in which Y is hydrogen, can be prepared by coupling in approximately stoichiometric proportions a coupling component, Z, as defined in relation to Formula I, with a diazotized amino compound of Formula III in which Y is hydrogen. Similarly, an alternate method for preparing the dyestuffs of Formula II in which Y is hydrogen comprises coupling in approximately stoichiometric proportions a compound of Formula IV in which Y is hydrogen with a diazonium compound of the formula T—(N⁺=NAn⁻)_c wherein c, T and An have the same meanings as hereinbefore indicated. Although the intermediates of Formula III and IV in which Y is hydrogen can be separately prepared and isolated for use in preparing the dyestuffs of Formula I and Formula II in which Y is hydrogen, it is not necessary to do so. It is particularly convenient to first hydrolyze the acylated intermediates of Formula III or of Formula IV and to then proceed directly with the diazotization and coupling in the same reaction vessel.

When preparing the compounds of Formula I in which Y is hydrogen and Y¹ is



by hydrolysis of the corresponding dyestuffs of Formula I in which Y is —COR, it is preferred to hydrolyze those compounds in which R is hydrogen or equivalently in which Y is formyl. The formyl group is preferred because it is readily hydrolyzed with minimal concomitant hydrolysis of the remaining amide group. In the same sense

and for the same reason, it is preferred to employ those compounds of Formula III in which Y is formyl when Y¹ is

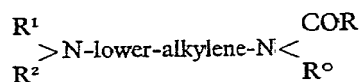


for the preparation of the corresponding intermediates of Formula III in which Y is hydrogen.

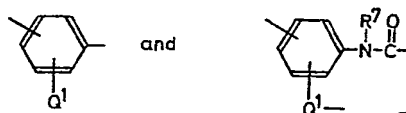
The water-soluble quaternary ammonium azo dyestuffs according to our invention may contain one or more primary amino groups in addition to the quaternary ammonium group. The said amino-basic dyestuffs can, of course, exist either in free base form or in acid-addition salt form. For the purpose of our invention, the two forms are full equivalents, because the dyestuffs are water-soluble in either form, and salt formation is believed not to affect the physical properties of the dyestuffs either adversely or beneficially.

The manner and process of making and using the quaternary ammonium azo dyestuffs of the invention, and the best mode contemplated by the inventors of carrying out this invention, will now be described so as to enable any person skilled in the art to which it pertains to make and use the same.

The intermediates of Formula III in which Y is —COR, are conveniently prepared in two steps, firstly by heating a halogeno-lower-alkylene-substituted nitrobenzene or a halogeno-lower-alkylene carboxylic acid N—R⁷-nitroanilide with a compound of the formula



in a suitable medium, for example a polar solvent, to obtain the nitro-substituted precursors of the intermediates of Formula III wherein Y¹ is

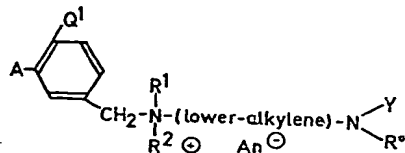


respectively.

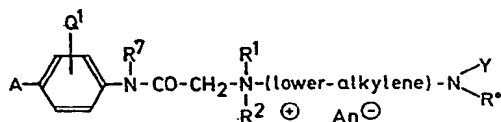
Quaternization is usually complete in from two to forty-eight hours, depending upon the nature of the reactants, the nature of the reaction medium, and the reaction temperature. The reaction generally proceeds readily at temperatures in the range 50—110°C. It is convenient to employ a reaction medium which boils within the specified range in order that the reaction temperature is maintained by merely refluxing the medium. Convenient media for carrying out the process according to this aspect of the invention include water; containing from 1 to 4 carbon atoms, for example methanol, ethanol and isopropyl alcohol; the lower-alkylene glycols, for example, ethylene glycol and propylene glycol; acetonitrile; and dimethylformamide. We generally prefer to use isopropyl alcohol or water as the reaction media because they have suitable boiling points and they are inexpensive. The N-R¹-N-[(lower-alkylene)¹-Y¹-NO₂]-N-R²-N-[(lower-alkylene)-NR⁰COR] ammonium halide thus obtained is then in the second step subjected to reduction of the nitro group to obtain the corresponding amino-substituted intermediates of Formula III in which Y is —COR. Reduction is carried out with powdered iron under essentially neutral conditions. The reduction generally proceeds readily in aqueous media at a temperature in the range 50—75°C. Alternatively, high-pressure, catalytic reduction is employed. We have found that when the latter method is used, reduction is conveniently and efficiently effected in aqueous media at approximately 600 pounds per square inch hydrogen pressure at a temperature between 60—80°C. Although any of the known poisoned reduction catalysts may be used, we prefer to use a platinum sulfide on charcoal catalyst.

The intermediates of Formula III in which Y is hydrogen are obtained by the hydrolysis of the corresponding compound of Formula III wherein Y is —COR. The hydrolysis is effectively accomplished by heating the acylamino intermediate in admixture with dilute aqueous acid as hereinbefore described.

Particularly preferred among the novel intermediates of Formula III and their corresponding precursors useful for the preparation of the dyestuffs of Formula I, are those compounds represented by the formula



5 and by the formula



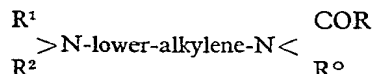
where in both formulas A is nitro or amino; R⁰ is hydrogen, lower-alkyl or hydroxy-lower-alkyl; Q¹ is hydrogen, lower-alkyl, lower-alkoxy or halogen; R¹ is lower-alkyl, lower-alkenyl or hydroxy-lower-alkyl; R² is lower-alkyl, lower-alkenyl, hydroxy-lower-alkyl or -(lower-alkylene)-NR⁰Y or R¹ and R² together with the nitrogen atom to which they are commonly attached, are pyrrolidine, piperidine or 4-lower-alkanoyl

10 piperazine; Y is hydrogen or $\text{—}\overset{\text{O}}{\parallel}\text{C—R}$ wherein R is hydrogen, lower-alkyl, lower-alkenyl, phenyl or phenyl-lower-alkyl; An is an anion; and in the latter formula R⁷ is hydrogen or lower-alkyl.

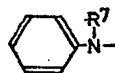
15 The halide quaternizing agents used as starting materials for preparing the intermediate compounds of Formula III are generally known classes of compounds, and are readily prepared by methods well-known in the art. For example, the halogeno-lower-alkylene-substituted nitro-benzenes are prepared by causing hydroxy-lower-alkylene-substituted nitrobenzenes to react with a hydrogen halide or a hydrogen

20 halide-producing reactant, for example phosphorous oxychloride. The halogeno-lower-alkylene carboxylic acid N-R⁷-nitroanilides are prepared, for example, by interaction of a halogen-substituted alkanoyl halide with an N-R⁷ substituted nitroaniline. The carboxylic acylamino-lower-alkylamines are prepared as hereinbefore described.

25 The compounds of Formula IV in which Y is —COR, are conveniently prepared by heating an N-R⁷-N-(halo-lower-alkylene)-substituted aniline with a compound of the formula



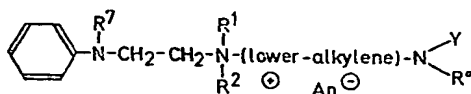
to obtain the intermediate of Formula IV wherein Y² is



30 The reaction can be carried out without other media or in a suitable medium for example, a polar solvent. Quaternization is usually complete in from two to forty-eight hours and proceeds readily at temperatures in the range of 50—110°C. Convenient media for carrying out the process according to this aspect of the invention include water; alcohols containing from 1 to 6 carbon atoms, for example, methanol, ethanol and isopropyl alcohol; the lower-alkylene glycols, for example, ethylene glycol and propylene glycol; acetonitrile and dimethylformamide.

35 Those intermediates represented by Formula IV in which Y is hydrogen are conveniently obtained by the hydrolysis of the corresponding acylamino compound of Formula IV wherein Y is —COR. The hydrolysis is accomplished by heating the acylamino intermediate in admixture with dilute aqueous acid as hereinbefore described.

40 Novel intermediates that are particularly preferred and useful for the preparation of the dyestuffs of Formula II and which are within the ambit of Formula IV, are those compounds represented by the formula



in which R^o is hydrogen, lower-alkyl or hydroxy-lower-alkyl; R¹ is lower-alkyl, lower-alkenyl or hydroxy-lower-alkyl; R² is lower-alkyl, lower-alkenyl, hydroxy-lower-alkyl or -(lower-alkylene)-NR^oY or R¹ and R² together with the nitrogen atom to which they are commonly attached are pyrrolidine, piperidine or 4-lower-alkanoyl piperazine; R⁷

is hydrogen or lower-alkyl; Y is hydrogen or $\text{—}\overset{\text{O}}{\underset{\parallel}{\text{C}}}\text{—R}$ wherein R is hydrogen, lower-alkyl, lower-alkenyl, phenyl or phenyl-lower-alkyl; and An is an anion.

The halide quaternizing agents required for preparing the intermediate compounds of Formula IV are generally-known classes of compounds and are conveniently prepared by methods well-known in the art. For example, the N-R¹-N-(halo-lower-alkylene)-substituted anilines are prepared by causing an N-R⁷-N-(hydroxy-lower-alkylene)-substituted aniline to react with a hydrogen halide. The carboxylic-acylamino-lower-alkyl-amines are prepared as hereinbefore described.

The new water-soluble quaternary ammonium-substituted dyestuffs of Formulas I and II disclosed herein are useful dyestuffs which can be applied to natural fibers, to fiber-forming synthetic materials and to cellulosic materials by methods conventional in the dyeing art since it has been found that the dyestuffs of this invention are substantive to wool, silk, nylon, rayon, polyacrylonitrile, cotton and paper. The dyed products thus obtained are stable to ultra-violet light and to washing. The novel dyes are especially valuable for imparting various shades of a stable red or yellow color to cotton and to paper, both sized and unsized. For use in the paper trade, our dyes have several outstanding advantages over quaternary ammonium dyes in the prior art. First, our dyes are less prone to "bleed" when paper impregnated with the dyes is wet and placed in contact with moist white paper. This is a particularly desirable property for dyes designed for coloring paper to be used in facial tissues or napkins, wherein it can be foreseen that the colored paper, while wet, may come in contact with other surfaces, such as textiles or paper, which should be protected from stain. Another advantageous property of our new dyes for use in the paper trade is found in their high degree of color discharge when bleached with hypochlorite or "chlorine" bleach. This property of dyes is particularly desired by papermakers in order that dyed paper may be completely bleached prior to reprocessing. Still another advantageous property of our dyestuffs is found in their high resistance to a change of shade when used to color cellulosic materials, which have either previously been treated with or are treated subsequent to dyeing, with wet-strength resin.

The carboxylic-acylamino compounds and the free amino compounds of the instant invention are substantially equal with respect to their bleachability. With respect to shade, in general, the free amino compounds have slightly deeper shades than the carboxylic acylamino compounds. Presumably because of the availability of the free amino group to bond with the fiber and wet-strength resin or similar paper additives, the free amino compounds are, in general, less prone to bleed than are the carboxylic acyl-amino compounds both when wet with water alone and in the presence of soap.

The structures of the novel compounds herein disclosed were established by their mode of synthesis and analysis of their infra-red absorption spectra, and were corroborated by the correspondence of calculated and found values of elemental analyses of representative samples.

Our invention is further illustrated by the following procedures and Examples, which are given for the purpose of illustration only, and not to limit the invention thereto. All parts are parts by weight.

PREPARATION OF INTERMEDIATES

A. N-R¹-N-[(lower-alkylene)¹-Y¹NH₂]-N-R²-N-[(lower-alkylene)-NR^oY]
quaternary ammonium intermediates (Formula III)

1. N,N-Dimethyl-N-(3-amino-4-methoxybenzyl)-N-3-formamidopropyl-ammonium chloride

a.) To a refluxing solution of 35.4 parts of N-(3-dimethylaminopropyl)formamide in 40 parts of isopropyl alcohol there was added over a two hour period 50.4 parts of 4-methoxy-3-nitrobenzyl chloride. Refluxing was continued for four hours after which the reaction mixture was diluted with 100 parts of isopropyl alcohol and cooled to 20°C. The solid that separated was collected and washed with a small amount of fresh isopropyl alcohol and then dried in a vacuum oven to yield 71.1 parts of N,N-dimethyl-N-(3-nitro-4-methoxybenzyl)-N-3-formamidopropyl-ammonium chloride, as a cream colored solid which melted at 180—183°C.

b.) A mixture of 30.0 parts of iron powder, 6.0 parts of sodium acetate, and 120 parts of water was heated to 50°C. Heating was stopped and 33.1 parts of N,N - dimethyl - N - (3 - nitro - 4 - methoxybenzyl) - N - 3 - formamidopropylammonium chloride was added over a period of two and a half hours at a rate such as to maintain the temperature at 50—55°C. At the end of the addition, heating was resumed at 50—55°C. for two hours. The reaction mixture was cooled to 25°C. and filtered with the aid of diatomaceous earth to obtain a pale yellow solution. A sample of the solution was analyzed for free amine content by diazotization using a standardized sodium nitrite solution. The analytical results indicated that N,N-dimethyl-N-(3-amino-4-methoxybenzyl)-N-3-formamidopropylammonium chloride was obtained in nearly quantitative yield. The product was used directly in the form of its aqueous solution without isolation.

c.) A mixture of 166 parts of N,N-dimethyl-N-(3-nitro-4-methoxybenzyl)-N-3-formamidopropylammonium chloride, 200 parts of water, and 3 parts of a 5 per cent platinum sulfide on charcoal mixture was subjected to 600 pounds per square inch of hydrogen at 70—75°C. After two and one-third hours, when the total up take of hydrogen was approximately 92% of theory, absorption of hydrogen ceased. The reaction mixture was cooled and filtered with the aid of diatomaceous earth. A sample of the filtrate was analyzed for free amine content by diazotization using a standardized sodium nitrite solution. The results indicated that N,N - dimethyl - N - (3 - amino - 4 - methoxybenzyl) - N - 3 - formamidopropylammonium chloride was obtained in nearly quantitative yield. The product was used directly in the form of an aqueous solution without isolation.

2. *N,N - Dimethyl - N - (3 - amino - 4 - methoxybenzyl) - N - 3 - benzamido-propylammonium chloride*

Proceeding in a manner similar to that described above in 1a, and using N-(3-dimethylaminopropyl)benzamide, and 3 - nitro - 4 - methoxybenzyl chloride, there was obtained N,N - dimethyl - N - (3 - nitro - 4 - methoxybenzyl) - N - 3 - benzamido-propylammonium chloride, as an off white solid which melted at 133—136°C.

When the N,N - dimethyl - N - (3 - nitro - 4 - methoxybenzyl) - N - 3 - benzamidopropylammonium chloride thus obtained is subjected to reduction by either of the methods of 1b or 1c above, there is obtained an aqueous solution of N,N-dimethyl - N - (3 - amino - 4 - methoxybenzyl) - N - 3 - benzamidopropylammonium chloride.

3. *N - Methyl - N - (3 - amino - 4 - methoxybenzyl) - N,N - bis (3 - formamido-propyl)ammonium chloride.*

a.) A mixture of 54.0 parts of N,N-bis(3-formamidopropyl)methylamine, 50.4 parts of 4-methoxy-3-nitrobenzyl chloride, and 78 parts of acetonitrile was stirred at reflux for seven and a half hours. An additional 78 parts of acetonitrile was added to the reaction mixture causing an oil to separate. Heating at reflux was continued for an additional two hours and the 140 parts of acetonitrile was distilled away and 200 parts of water was added. The remaining acetonitrile was removed by distillation and the cooled reaction mixture was filtered with the aid of diatomaceous earth to obtain an aqueous solution of N - methyl - N - (3 - nitro - 4 - methoxybenzyl) - N,N - bis(3-formamidopropyl)ammonium chloride. The solution was used directly for reduction of the nitro group.

b.) Proceeding in a manner similar to that described above in 1b, and using 75 parts of iron powder and 15.0 parts of sodium acetate, the N - methyl - N - (3 - nitro - 4 - methoxybenzyl) - N,N - bis(3 - formamidopropyl)ammonium chloride obtained in the form of its aqueous solution from 3a above was reduced to obtain 61 parts of N - methyl - N - (3 - amino - 4 - methoxybenzyl) - N,N - bis(3 - formamido-propyl)ammonium chloride in the form of an aqueous solution.

4. *N - Methyl - N - (3 - amino - 4 - methoxybenzyl) - N,N - bis(3 - amino-propyl)ammonium chloride trihydrochloride*

N - Methyl - N - (3 - amino - 4 - methoxybenzyl) - N,N - bis(3 - formamido-propyl)ammonium chloride obtained in 3b above was hydrolyzed by heating in a refluxing solution of 63 parts of water containing 24 parts of concentrated hydrochloric acid during two hours to obtain an aqueous solution of N - methyl - N - 3 - (amino-4 - methoxybenzyl) - N,N - bis - (3 - aminopropyl)ammonium chloride trihydrochloride.

5. *N,N - Dimethyl - N - (4 - aminophenyl)carbamylmethyl - N - 3 - formamido-propylammonium chloride.*

a.) In a manner similar to that described above in 1a, and using 14.2 parts of N - (3 - dimethylaminopropyl)formamide, 20.0 parts of 2 - chloro - 4' - nitro-acetanilide, and 78 parts of isopropyl alcohol there was obtained 27.4 parts of N,N-

10

dimethyl - N - (4 - nitrophenyl)carbanylmethyl - N - 3 - formamidopropyl - ammonium chloride as a white solid which melted at 195—196°C.

b.) Proceeding in a manner similar to that described above in 1b, and using 68.8 parts of N,N - dimethyl - N - (4 - nitro - phenyl)carbanylmethyl - N - 3 - formamidopropylammonium chloride obtained above in 3a, 60.0 parts of iron powder, 12.0 parts of sodium acetate, and 250 parts of water there was obtained an aqueous solution of 33.0 parts of N,N - dimethyl - N - (4 - aminophenyl)carbanylmethyl - N - 3 - formamidopropylammonium chloride.

c.) Following the procedure described in 1c above, N,N - dimethyl - N - (4 - nitrophenyl)carbanylmethyl - N - 3 - formamido - propylammonium chloride was catalytically hydrogenated in aqueous solution at 70—75°C. and at 600 pounds per square inch in the presence of a 5 per cent platinum sulfide on charcoal mixture to obtain an aqueous solution of N,N - dimethyl - N - (4 - aminophenyl)carbanylmethyl - N - 3 - formamidopropylammonium chloride.

6. *N,N - Dimethyl - N - (4 - aminophenyl)carbanylmethyl - N - 3 - aminopropyl - ammonium chloride hydrochloride*

A solution of 10.0 parts of N,N - dimethyl - N - (4 - nitrophenyl)carbanylmethyl - N - 3 - formamidopropylammonium chloride in 100 parts of water containing 6.0 parts of concentrated hydrochloric acid was heated for about two hours. The reaction mixture was rendered slightly alkaline by the addition of 50 per cent aqueous sodium hydroxide and stored in the refrigerator for two days. The reaction mixture was then filtered to remove a small amount of solid and the filtrate was acidified with 48 parts of concentrated hydrochloric acid. Acetone was slowly added to the acidified filtrate until precipitation started. When precipitation of the product was complete, the solid was collected on a filter, washed with acetone, and dried at 75°C. to obtain 8.2 parts of N,N - dimethyl - N - (4 - nitrophenyl)carbanylmethyl - N - 3 - aminopropyl - ammonium chloride as the mono-hydrochloride salt, a white solid which melted at 244—245°C.

When the N,N - dimethyl - N - (4 - nitrophenyl)carbanylmethyl - N - 3 - aminopropylammonium chloride hydrochloride thus obtained is neutralized with dilute alkali and then subjected to reduction according to the procedure of 1b above, there is obtained an aqueous solution of N,N - dimethyl - N - (4 - aminophenyl)carbanylmethyl - N - 3 - aminopropyl - ammonium chloride.

7. *N,N - Dimethyl - N - (3 - amino - 4 - methoxybenzyl) - N - 3 - aminopropyl - ammonium chloride*

When N,N - dimethyl - N - (3 - amino - 4 - methoxybenzyl) - N - 3 - formamidopropylammonium chloride obtained in 1b or 1c above is hydrolyzed by heating in a dilute aqueous solution of hydrochloric acid according to the procedure of 4 above, there is obtained an aqueous solution of N,N - dimethyl - N - (3 - amino - 4 - methoxybenzyl) - N - 3 - aminopropylammonium chloride as the dihydrochloride salt.

In addition to those for which detailed preparations are given above, the following N - R¹ - N - [(lower - alkylene)¹ - Y¹NH₂] - N - R² - N - [(lower - alkylene) - NR^oY] quaternary ammonium intermediates are obtained in aqueous solution when the indicated nitrophenyl-substituted quaternizing agent is interacted with the indicated tertiary amino compound according to a procedure similar to those given under 1a, 2, 3a, and 5a and the resulting nitro-substituted compound is reduced by a procedure similar to those given under 1b or 1c:

N,N - Dimethyl - N - 2 - (3 - amino - 4 - methylphenyl)ethyl - N - 3 - formamidopropylammonium chloride starting with N - (3 - dimethylaminopropyl)formamide and 2 - (4 - methyl - 3 - nitrophenyl)ethyl chloride;

N - Methyl - N - 3 - (4 - aminophenyl)propyl - N,N - bis(3 - formamidopropyl) - ammonium chloride starting with N,N - bis(3 - formamidopropyl) - methylamine and 3-(4-nitrophenyl)propyl chloride;

N,N - Diethyl - N - 6 - (3 - amino - 4 - methoxyphenyl)hexyl - N - 3 - formamidopropylammonium chloride starting with N - (3 - diethylaminopropyl)formamide and 6 - (4 - methoxy - 3 - nitrophenyl)hexyl chlorides;

N,N - Dimethyl - N - 2 - ethyl - 4 - (3 - amino - 5 - chlorophenyl)butyl - N - 3 - benzamidopropylammonium chloride starting with N - (3 - dimethylaminopropyl) - benzamide and 2 - ethyl - 4 - (3 - chloro - 5 - nitrophenyl) - butyl chloride;

N,N - Dimethyl - N - 1 - methyl - 3 - (4 - amino - 3 - bromophenyl) - propyl - N - 3 - acetamidopropylammonium chloride starting with N - (3 - dimethylaminopropyl) - acetamide and 1 - methyl - 3 - (3 - bromo - 4 - nitrophenyl)propyl chloride;

N,N - Diethyl - N - 3 - (4 - amino - 2 - chlorophenyl)carbanylmethyl - N - 4 - formamidobutylammonium chloride starting with N - (4 - diethylamino - 1 - methyl - butyl)formamide and 2',4' - dichloro - 4' - nitrobutyranilide;

- N,N - Dimethyl - N - (N - methyl - 4 - amino - 2 - chlorophenylcarbamy)-
methyl - N - 3 - phthalamidopropylammonium chloride starting with N - (3 - dimethyl-
aminopropyl)phthalamic acid and 2,2' - dichloro - N - methyl - 4' - nitroacetanilide;
- 5 N,N - Bis(2 - hydroxyethyl) - N - (3 - amino - 4 - methoxybenzyl) - N - 3 -
formamidopropylammonium chloride starting with N - (3 - diethanolaminopropyl)-
formamide and 4 - methoxy - 3 - nitrobenzyl chloride; 5
- 10 1 - [2 - (3 - Amino - 4 - methylphenyl)ethyl] - 1 - (2 - formamidoethyl) - 4 -
formylpiperazinium chloride starting with N - [2 - (4 - formylpiperazinoethyl)]form-
amide and 2 - (4 - methyl - 3 - nitrophenyl)ethyl chloride; 10
- N - Ethyl - N - 1 - methylbutyl - N - [2 - (2 - ethyl - 4 - aminophenylcarbamy)-
ethyl] - N - 2 - propionamidoethylammonium chloride starting with N - [2 - (N-
ethyl - N - 1 - methylbutyl)aminoethyl]propionamide and 3 - chloro - 2' - ethyl - 4' -
nitropropionanilide;
- 15 N,N - Dimethyl - N - 3 - (4 - aminophenyl)propyl - N - 6 - iso - butyramidoethyl-
ammonium chloride starting with N - (6 - dimethylaminoethyl)iso - butyramide and
3 - (4 - nitrophenyl)propyl chloride; 15
- N - Methyl - N - ethyl - N - 3 - (4 - aminophenyl)propyl - N - 2 - (N - methyl-
propionamido)ethylammonium bromide starting with N - methyl - N - [2 - (N -
ethyl - N - methyl)aminoethyl]propionamide and 3 - (4 - nitrophenyl)propyl bromide;
- 20 N,N - Dimethyl - N - (3 - amino - 4 - methoxybenzyl) - N - 3 - [N - (3 -
hydroxypropyl)formamido - propylammonium iodide starting with N - (3 - hydroxy-
propyl) - N - (3 - dimethylaminopropyl)formamide and 3 - nitro - 4 - methoxybenzyl-
iodide; 20
- N - Methyl - N - 2 - (4 - methyl - 3 - aminophenyl)ethyl - N,N - bis [3 - (N-
methylformamido)propyl]ammonium bromide starting with N,N - bis[3 - (N -
methylformamido)propyl]methylamine and 2 - (4 - methyl - 3 - nitrophenyl)ethyl
bromide; 25
- N - (3 - Amino - 4 - methoxybenzyl) - N - 2 - (N - isopropylacrylamido)ethyl-
piperidinium chloride starting with N - isopropyl - N - (2 - piperidinoethyl)acrylamide
and 4 - methoxy - 3 - nitrobenzyl chloride; 30
- 30 N,N - Di - n - propyl - N - (4 - amino - N - methyl - 2 - chlorophenylcarbamy)-
methyl - N - 1 - methyl - 2 - (N - ethyl - p - nitrobenzamido)ethylammonium
chloride starting with 2,2' - dichloro - N - methyl - 4' - nitroacetanilide and N - ethyl-
N - (2 - di - n - propylamino - 2 - methylethyl)p - nitrobenzamide; 30
- 35 N - Methyl - N - 2 - (N - methylacetamido)ethyl - N - 2 - ethyl - 4 - (3 - chloro-
4 - aminophenyl)butyl - N - 3 - (N - methylacetamido)propylammonium chloride
starting with N - [3 - (N - methylacetamido)propyl] - N - [2 - (N - methylacetamido)-
ethyl]methylamine and 2 - ethyl - 4 - (3 - chloro - 5 - nitrophenyl)butyl chloride; 35
- 40 N - (4 - Amino - N - methyl - 2 - chlorophenylcarbamy)methyl - N - 3 - (N-
methyl - n - valeramido)propylpyrrolidinium chloride starting with N - methyl - N -
(3-pyrrolidinylpropyl)valeramide and 2,2' - di - chloro - N - methyl - 4' - nitro -
acetanilide; 40
- N - Allyl - N - ethyl - N - 6 - (N - ethyl - 4 - aminophenylcarbamy) - hexyl -
N - 2 - (4 - chlorobenzamido)ethylammonium chloride starting with N - [2 - (N-
allyl - N - ethyl)aminoethyl]p - chlorobenzamide and 7 - chloro - N - ethyl - 4' -
nitroheptanoanilide; 45
- 45 N - Methyl - N - 2 - (N - n - propyl - 4 - aminophenylcarbamy) - 2 - n - propyl-
ethyl - N - 2 - acetamidoethyl - N - 3 - acetamidopropylammonium chloride starting
with N - [3 - (N - methyl - N - 2 - acetamidoethyl)aminopropyl]acetamide and
3 - chloro - N - 2 - di(n - propyl) - 4' - nitropropionanilide; 50
- 50 N - (3 - Amino - 4 - methoxybenzyl) - N - 2 - acrylamidoethylpiperidinium
chloride starting with N - (2 - piperidinoethyl)acrylamide and 4 - methoxy - 3 - nitro-
benzyl chloride; 50
- 55 N - n - Butyl - N - isopropyl - N - [4 - (3 - amino - 4 - isobutylphenylcarbamy)] -
n - butyl - N - phenylacetamidoethylammonium chloride starting with N - [2 - (N-
n - butyl - N - isopropyl)aminoethyl]phenylacetamide and 5 - chloro - 4' - iso - butyl-
3'-nitrovalerylalilide; 55
- 60 N - (4 - Amino - N - methyl - 2 - chlorophenylcarbamy)methyl - N - 3 - n -
valeramido)propylpyrrolidinium chloride starting with N - (3 - pyrrolidinylpropyl)-
valeramide and 2,2' - dichloro - N - methyl - 4' - nitroacetanilide; 60
- N,N - Diallyl - N - 1 - methyl - 3 - (4 - amino - 3 - bromophenyl) - propyl - N -
2 - phenylpropionamidoethyl ammonium chloride starting with N - (2 - diallylamino-
ethyl)phenylpropionamide and 1 - methyl - 3 - (3 - bromo - 4 - nitrophenyl)propyl
chloride;

12

N,N - Diethyl - N - 2,2 - dimethyl - 2 - (4 - amino - 2 - n - butoxyphenyl)carbamyl)ethyl - N - 5 - (2 - methylacrylamidopentyl)ammonium chloride starting with N - (2 - diethylaminopentyl) - 2 - methylacrylamide and 3 - chloro - 2,2 - dimethyl - 2' - n - butoxy - 4' - nitropropionanilide;

5 N,N - Diisopropyl - N - 2 - ethyl - 4 - (5 - amino - 3 - chlorophenyl) - butyl - N - 2 - (4 - methoxybenzamido)ethylammonium chloride starting with N - (2 - diisopropylaminoethyl) - p - methoxybenzamide and 2 - ethyl - 4 - (3 - chloro - 5 - nitrophenyl)butyl chloride;

10 N,N - Diisopentyl - N - 5 - (5 - amino - 2 - propoxyphenylcarbamyl) - pentyl - N - 2 - butyramidoethylammonium chloride starting with N - (2 - diisopentylaminoethyl)butyramide and 6 - chloro - 2' - n - propoxy - 5' - nitrohexanoanilide;

N,N - Dihexylamino - N - 6 - (3 - amino - 4 - methoxyphenyl) - hexyl - N - 2 - n - caproamidoethylammonium chloride starting with N - (2 - dihexylaminoethyl) - n - caproamide and 6 - (4 - methoxy - 3 - nitrophenyl) - hexyl chloride;

15 N,N - Diisobutyl - N - 2 - (3 - amino - 4 - methylphenyl)ethyl - N - 6 - acetamidohexylammonium chloride starting with N - (6 - diisobutylaminoethyl) - acetamide and 2 - (4 - methyl - 3 - nitrophenyl)ethyl chloride;

20 N,N - Diethyl - N - 1 - methyl - 3 - (3 - bromo - 4 - aminophenyl) - propyl - N - 3 - methyl - 3 - acrylamidopropylammonium chloride starting with N - (1 - methyl - 3 - diethylaminopropyl)acrylamide and 1 - methyl - 3 - (3 - bromo - 4 - nitrophenyl) - propyl chloride;

N,N - Di - n - propyl - N - (3 - amino - 4 - methoxybenzyl - N - 1 - methyl - 2 - (p - nitrobenzamido)ethylammonium chloride starting with N - (2 - di - n - propylamino - 2 - methylethyl) - p - nitrobenzamide and 4 - methoxy - 3 - nitrobenzyl chloride.

25 N,N - Bis(2 - hydroxyethyl) - N - 2 - (N - n - propyl - 4 - aminophenylcarbamyl) - 2 - n - propylethyl - N - 2,2 - dimethyl - 2 - benzamidoethylammonium chloride starting with N - (2 - diethanolamino - 1,1 - dimethylethyl) - phenylacetamide and 3 - chloro - N - 2 - di(n - propyl) - 4' - nitropropionanilide;

30 N - Methyl - N - isopropyl - N - 2 - ethyl - 4 - (3 - chloro - 4 - aminophenyl) - butyl - N - 3 - salicylamidopropylammonium chloride starting with N - [3 - (N - isopropyl - N - methyl)aminopropyl]salicylamide and 2 - ethyl - 4 - (3 - chloro - 5 - nitrophenyl) - butyl chloride; and

35 The foregoing N - R^1 - [(lower - alkylene)¹ - Y^1NH_2] - N - R^2 - N - [(lower - alkylene)² - NR^2COR] ammonium halide intermediates are of course, useful for preparing the compounds of Formula I in which Y is —COR. In addition, they may be hydrolyzed by a procedure similar to that in A 4 hereinabove to obtain the corresponding N - R^1 - N - [(lower - alkylene)¹ - Y^1NH_2] - N - R^2 - N - [(lower - alkylene)² - NR^2Y] ammonium halide intermediates which are useful for and afford an alternate method for preparing the final products of Formula I in which Y is hydrogen.

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B. N - R^1 - N - [(lower - alkylene)¹ - Y^2 - H] - N - R^2 - N - [(lower - alkylene)² - NR^2Y] ammonium halide intermediates (Formula IV).

1. N,N - Dimethyl - N - 2 - (N' - ethylanilino)ethyl - N - 3 - formamidopropylammonium chloride

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A stirred mixture of 157 parts of N - (3 - dimethylaminopropyl)formamide in 20.0 parts of water was heated to 80°C. and over a period of one and one half hours there was added 171 parts of N - ethyl - N - (2 - chloroethyl)aniline. The reaction mixture was heated at 95—100°C. until a small sample when diluted with water gave a clear solution. After about seven hours of heating at 95—100°C. there was obtained

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N,N - dimethyl - N - 2 - (N' - ethylanilino) - ethyl - N - 3 - formamidopropylammonium chloride in the form of an aqueous solution.

2. N,N - Dimethyl - N - 2 - (N' - ethylanilino)ethyl - N - 3 - aminopropylammonium chloride

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Dilute hydrochloric acid hydrolysis of N,N - dimethyl - N - 2 - (N' - ethylanilino)ethyl - N - 3 - formamidopropylammonium chloride following a procedure similar to that of A-4 above gives an aqueous solution of N,N - dimethyl - N - 2 - (N' - ethylanilino)ethyl - N - 3 - aminopropylammonium chloride.

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When the indicated *tert.* amino compound is quaternized with the indicated N - R^1 - N - (halo - lower - alkylene) - substituted aniline or aminonaphthalene according to a procedure similar to that of B-1 above, the following N - R^1 - N - [(lower - alkylene)¹ - Y^2 - H] - N - R^2 - N - [(lower - alkylene)² - NR^2COR] ammonium halide intermediates are obtained in aqueous solution:

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- N - Ethyl - N - 1 - methylbutyl - N - 4 - (N - ethylanilino)butyl - N - 2 - propionamidoethylammonium chloride from N - [2 - (N - ethyl - N - 1 - methylbutyl)-aminoethyl]propionamide and N - ethyl - N - (4 - chlorobutyl) - aniline;
- 5 N,N - Dimethyl - N - 3 - ethyl - 4 - (N - methylanilino)butyl - N - 6 - isobutyramidoethylammonium chloride from N - (6 - dimethylaminoethyl) - iso - butyramide and N - methyl - N - (2 - ethyl - 4 - chlorobutyl) - aniline;
- 10 N - 6 - (N - propylanilino)hexyl - N - 2 - acrylamidoethylpiperidinium chloride from N - (2 - piperidinoethyl)acrylamide and N - n - propyl - N - (6 - chlorohexyl)-aniline;
- 15 N - 2 - (N - Ethylanilino)ethyl - N - 3 - valeramidopropylpyrrolidinium chloride from N - (3 - pyrrolidinylpropyl)valeramide and N - ethyl - N - (2 - chloroethyl)aniline;
- 20 N,N - Diallyl - N - 2,2 - dimethyl - 3 - anilinopropyl - N - 2 - phenyl - propionamidoethylammonium chloride from N - (2 - diallylaminoethyl) - phenylpropionamide and N - (2,2 - dimethyl - 3 - chloropropyl)aniline;
- 25 N,N - Diethyl - N - 3 - (2 - naphthylamino)propyl - N - 3 - methyl - 3 - acrylamidopropylammonium chloride from N - (1 - methyl - 3 - diethyl - aminopropyl)-acrylamide and N - (3 - chloropropyl) - 2 - naphthylamine;
- 30 N,N - Bis(2 - hydroxyethyl) - N - 5 - (N - isopentylanilino)pentyl - N - 2,2 - dimethyl-2-phenylacetamidoethylammonium chloride from N-(2-diethanolamino-1,1-dimethylethyl)phenylacetamide and N-isopentyl-N-(5-chloropentyl)aniline;
- 35 N - Methyl - N - isopropyl - N - 5 - (N - methyl - 1 - naphthylamino) - pentyl - N - 3 - salicylamidopropylammonium chloride from N - [3 - (N - isopropyl - N - methyl)aminopropyl]salicylamide and N - methyl - N - (5 - chloropentyl) - 1 - naphthylamine;
- 40 N - Methyl - N - 3 - formamidopropyl - N - 2 - (N - tert. - butyl - 2 - naphthylamino)ethyl - N - 3 - formamidopropylammonium chloride from N,N - bis(3 - formamidopropyl)methylamine and N - tert. - butyl - N - (2 - chloroethyl) - 2 - naphthylamine;
- 45 N - Methyl - N - 4 - (N - ethylanilino)butyl - N - 2 - acetamidoethyl - N - 3 - acetamidopropylammonium chloride from N - [3 - (N - methyl - N - 2 - acetamidoethyl)aminopropyl]acetamide and N - ethyl - N - (4 - chlorobutyl)aniline;
- 50 N,N - Dimethyl - N - 4 - (N - ethylanilino)butyl - N - 3 - [N - (3 - hydroxypropyl)formamido]propylammonium chloride from N - (3 - hydroxypropyl) - N - (3 - dimethylaminopropyl)formamide and N - ethyl - N - (4 - chlorobutyl)aniline;
- 55 N - Methyl - N - 3 - ethyl - 4 - (N - methylanilino)butyl - N,N - bis - [3 - (N - methylformamido)propyl]ammonium chloride from N,N - bis[3 - (N - methylformamido)propyl]methylamine and N - methyl - N - (2 - ethyl - 4 - chlorobutyl)aniline; and
- 60 N,N - Di - n - propylamino - N - 2,2 - dimethyl - 3 - anilinopropyl - N - 1 - methyl - 2 - (N - ethyl - p - nitrobenzamido)ethylammonium bromide from N - ethyl - N - (2 - di - n - propylamino - 2 - methylethyl)p - nitrobenzamide and N - (2,2 - dimethyl - 3 - chloropropyl)aniline.
- The foregoing N - R¹ - N - [(lower - alkylene)¹ - Y² - H] - N - R² - N - [(lower - alkylene)NR³COR]ammonium halide intermediates can of course, be used directly to produce the compounds of Formula II in which Y is —COR. Additionally, they may be hydrolyzed by a procedure similar to that described in A-4 hereinabove to obtain the corresponding N - R¹ - N - [(lower - alkylene)¹ - Y² - H] - N - R² - N - [(lower - alkylene)NR³H]ammonium halide intermediates which are useful for and afford an alternate method for preparing the final products of Formula II in which Y is hydrogen.

Testing Procedures

- The following test procedures were employed to determine the relative shades of the dyestuffs produced and to determine the resistance of the dyestuffs to bleed in moist paper, bleed from paper in the presence of soap, and to bleaching with hypochlorite bleach.

Shade

- Chromaticity values of dominant wavelength and excitation purity are determined by measuring the reflectance tristimulus values of dyed handsheet paper on a General Electric recording spectrophotometer in combination with a "Librascope" (trade mark) automatic tristimulus integrator and plotting the points on a chromaticity diagram according to the procedure described by A. C. Hardy, "Handbook of Colorimetry", The Technology Press, Massachusetts Institute of Technology, Cambridge, Massachusetts, 1936.

The dominant wavelength is a measure of the shade imparted to the paper by the dye, and the excitation purity is a measure of the saturation or depth of the color. Inasmuch as the eye is more sensitive to minor variations in color than the most sensitive instrument, the shades imparted to test papers were also compared visually.

In some cases absorbance of aqueous solutions in the visible light region were measured by standard methods on a Perkin-Elmer Model 4000A Spectracord.

Water "Bleed" Test

This procedure is a modification of the AATCC Standard Test Method 15-1962, "Colorfastness to Perspiration".

Test pieces $1\frac{1}{8}$ inch in diameter (approximately one square inch area) are cut from the dyed paper to be tested and marked, with lead pencil, to indicate sample and wire (or felt) side. One or more dyed papers of known dye migration quality are included in the test series as standards.

The absorbent material consists of filter paper having at least one side with smooth finish (Eaton-Dikeman No. 613, or equivalent) cut to 2 inch by 3 inch rectangles. In addition, smooth, flat, glass or clear plastic plates of adequate stiffness, measuring $2\frac{1}{2}$ inches wide and 3 to $4\frac{1}{2}$ inches long, are required as separating plates. A 500 gram weight serves as a dead weight loading.

Two filter paper absorbent pieces are used for each dyed paper test circle, one for each side. These are marked on the smoother surface (with lead pencil) prior to beginning the test to indicate the sample and the sample surface (wire or felt) which it will contact.

The migration test "sandwich" is constructed as follows. A separating plate is placed on a horizontal support and one piece of the filter paper placed centrally on this plate with the smoother side up. The circular dyed paper test piece, held by tweezers, is immersed in water at room temperature for 3 seconds, drained for 3 seconds, and immediately centered on the filter paper, making sure that side (wire or felt) identifications are correct. Immediately, the second piece of filter paper, smoother side downward, is centered on the test circle and followed at one by another separating plate. This "sandwich" is pressed for a moment with the fingers, after which, without delay, a piece of filter paper is positioned on the top separating plate as before to receive a second test circle of wetted dyed paper. The above procedure is then repeated as rapidly as possible and without interruption, stacking one "sandwich" on the other, until all dyed paper test pieces have been put under test.

As soon as a stack is completed a 500 gram weight is centered on the top separating plate, and the assembly shrouded with moisture vapor resistant film to avoid undue drying. The stack is allowed to stand at room temperature for 4 hours, during which time ambient temperatures are occasionally recorded.

At the end of migration period the stack is disassembled, and each dyed paper test circle and its two filter paper absorbents clipped to a supporting card. A separate card is used for each test circle. The dyed paper test circles and filter paper are air dried at room temperature for at least two hours before ranking. Relative degrees of dye migration, as compared to that from standard samples, are determined by visual ratings, under Macbeth Northlight, of the intensity of dye stain on the filter paper surface which had been in contact with the test circle. Migration from the wire and felt sides are ranked separately.

Soap Bleed Test

This test compares the degree to which dyed papers will discolor a soap solution in which the paper is immersed.

A stock supply of soap solution containing 0.5% soap by weight is prepared by adding neutral white soap flakes (a mixture of 80 per cent sodium soap and 20 per cent potassium soap produced from 70 per cent tallow and 30 per cent coconut oil glyceride blend; "Ivory" (trade mark) brand, Proctor and Gamble Co.) slowly with stirring to hot tap water and then heated further with occasional stirring to 70—75°C.

Portions of 400 ml. of this solution are measured into 1,000 ml. beakers (one beaker for each test), covered with a watch glass, and allowed to cool to 60—65°C. At this point approximately 1.5 grams of the dyed paper (one half of a 3.0 gram, 8 inch square handsheet) is crumpled and immersed in its soap test solution.

Soaking is allowed to continue for 20 to 24 hours, with gradual cooling to room temperature. During this period the paper is squeezed by hand while submerged (or stirred vigorously with a glass rod) on at least three occasions during the first five hours, and again about one hour before ending the test period.

At the end of the immersion period the beaker contents are stirred and enough immediately screened through a double screen of 100 mesh stainless steel screening to nearly fill a two ounce, square clear glass bottle, which is then capped. These filtrates are then visually rated for color intensity under laboratory ceiling fluorescent tube lights.

Bleach Test

This procedure compares the degree to which the color of dyed or shaded papers would be discharged in a waste paper recovery operation employing hypochlorite bleach.

Test pieces measuring $\frac{3}{4}$ inch by $1\frac{1}{2}$ inch are die cut from the papers to be compared and identified, using lead pencil markings.

A stock supply of hypochlorite bleach is prepared by diluting commercial hypochlorite bleach (nominal available chlorine content, 5.0%) with distilled water to a concentration of 0.09 grams available chlorine per 100 ml. solution. Before diluting this solution to final volume the pH is adjusted with dilute sulfuric acid to pH 4.0 to 4.5.

Portions of 20 ml. each of the hypochlorite stock solution, at room temperature, are measured into test tubes 1 inch in diameter and 7 to 8 inches long, one tube for each test specimen. An extra such tube is prepared, fitted with a thermometer extending into the bleach solution, to follow the rise in bleach temperature.

One paper test piece is then dropped into each tube and submerged in the bleach liquor, adding all pieces as quickly as possible. The tubes are immediately stoppered and all simultaneously placed in a water bath previously heated to 54 to 56°C. (129 to 133°F.).

The test pieces are observed, especially during the very early minutes of bleaching, for obvious differences in the rate of color discharge. The temperature of the bleach liquors rises rapidly during the first 5 minutes.

While maintaining the water bath temperature in the 54 to 56°C. range, the bleach tubes remain, without agitation of the test pieces, in the water bath for 30 minutes. Occasional reading of the temperature of the "blank" bleach tube during this period are recorded.

At the end of this time all tubes are removed from the water bath, immediately filled with cold tap water, and the test pieces rinsed as quickly as possible, with cold tap water, into a large Buchner funnel (with no filter paper disk) where they are thoroughly washed with running cold tap water. The washed test pieces are finally placed on a blotter and air dried at room temperature.

The relative degree of bleaching is judged by visually ranking, under Macbeth Northlight, the intensity of residual color in the dry test pieces.

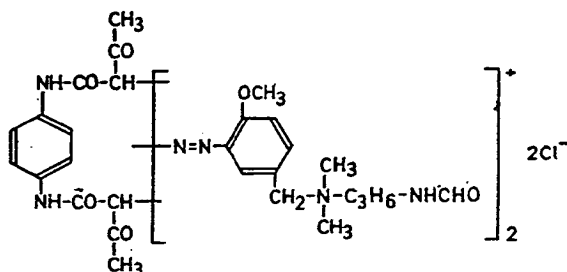
PREPARATION OF THE AROMATIC AZO DYESTUFFS

Example 1

A. To a solution of 30.8 parts of N,N - dimethyl - N - (3 - amino - 4 - methoxybenzyl) - N - 3 - formamidopropylammonium chloride in 130 parts of water at 0°C., there was added with stirring, 30 parts of concentrated hydrochloric acid. The amine was then diazotized at a temperature between 0—5°C. by adding 7.0 parts of solid sodium nitrite in small portions. The reaction mixture was stirred at less than 5°C. for ten minutes. The excess nitrite was then removed by the addition of an aqueous solution of sulfamic acid until nitrite ion could no longer be detected by testing with starch-iodide paper, and the mixture was made slightly alkaline to Congo red test paper by the addition of 20.0 parts of sodium acetate.

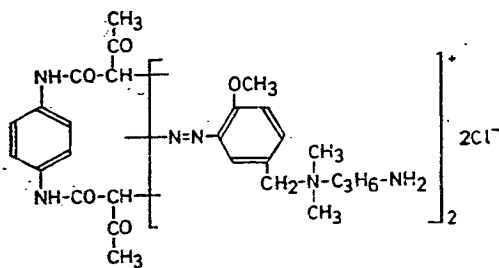
In a separate container, 13.4 parts of N,N' - diacetoacet - p - phenyldiamine, was mixed with sufficient 2-ethoxy ethanol to form a paste. The paste was slurried in 300 parts of water at 70°C. and to the slurry there was added with stirring 6.0 parts of a 50 per cent aqueous solution of sodium hydroxide. A solution resulted which was then added in a thin stream to the cold diazonium solution. The reaction mixture was stirred for four hours at 20°C. and then the resulting clear yellow solution was

evaporated to dryness to obtain chiefly a highly water-soluble yellow dyestuff having the formula



The visible absorption spectrum of an aqueous solution of this dyestuff, containing 0.10 g. of dye per liter of solution, showed a maximum at 399 milimicrons, $A = 1.275$. In the bleach test described above, paper dyed with this dyestuff was found to be highly bleachable. The dye was found to bleed slightly in the water-bleed test and in the soap bleed test.

B. A mixture of 6.0 parts of concentrated hydrochloric acid, 250 parts of water and 35 parts of the above product from A was heated at reflux for three hours. The mixture was cooled at 25°C. and the pH adjusted to 7.0 with aqueous alkali. Thus there was obtained in the form of an aqueous solution a yellow, highly water-soluble dyestuff of the formula



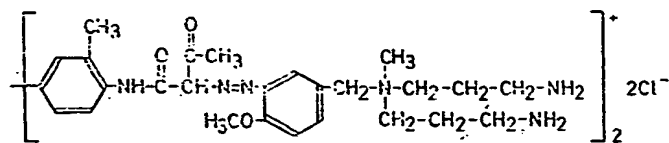
An aqueous solution of this dyestuff, containing 0.06 g. of dye per liter of solution, showed a maximum at 393.5 millimicrons, $A = 1.01$.

The bleachability properties of this dye were found to be essentially the same as for the formyl-substituted dyestuff of A. However, compared to said formyl-substituted dyestuff, this dyestuff exhibited significantly superior resistance to bleed in both the water bleed and the soap bleed tests.

Example 2

Following the procedure described above in Example 1, part B, 16.7 parts of N - methyl - N - (3 - amino - 4 - methoxybenzyl) - N,N - bis(3 - formamidopropyl) - ammonium chloride in a solution of 135 parts of water and 19 parts of concentrated hydrochloric acid was diazotized with 3.5 parts of sodium nitrite at 0°C. In a separate container, 9.1 parts of 4,4' - bis - o - acetoacetotoluidide (Naphthol AS - G) was mixed with sufficient 2 - ethoxy-ethanol to form a paste. The paste was slurred in 150 parts of water at 70°C. and to the slurry there was added with stirring 6 parts of a 50 per cent aqueous solution of sodium hydroxide. A solution resulted which was then added in a thin stream to the cold diazonium solution. The reaction mixture was allowed to warm to 30°C. and was then stirred for one hour after which it was heated at 60°C. for one hour. The reaction mixture, now a solution, was used directly for hydrolysis which was accomplished by the addition of 11.9 parts of concentrated hydrochloric acid followed by heating at reflux for three hours. The reaction mixture was then cooled and neutralized with a 50 per cent aqueous sodium hydroxide. There was thus obtained an aqueous

solution of a bright yellow, water-soluble dyestuff having the formula

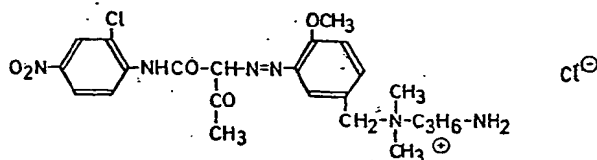


The visible absorption spectrum of an aqueous solution of this dyestuff containing 0.375 g. of dye per liter of solution had a maximum at 390 millimicrons, $A = 1.236$.

Paper dyed with this dyestuff in the bleach test hereinbefore described, was found to be readily bleachable. The dye was found to bleed slightly in the soap bleed and to about the same extent in the water bleed test.

Example 3

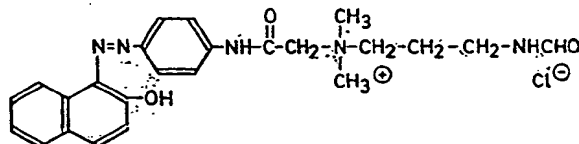
A solution of 7.5 parts of N,N - dimethyl - N - (3 - amino - 4 - methoxybenzyl)-N-3-formamidopropylammonium chloride in 40 parts of water containing 10 parts of concentrated hydrochloric acid was heated at reflux for two hours. To the solution which was chilled in an ice bath, there was then added an additional 1.2 parts of concentrated hydrochloric acid followed by the gradual addition of 1.75 parts of sodium nitrite. After stirring for ten minutes, excess nitrite was removed by the addition of an aqueous solution of sulfamic acid, and the solution was made neutral to Congo Red by the addition of sodium acetate. In a separate container there was prepared a coupler solution consisting of 6.4 parts of 2 - chloro - 4 - nitroacetanilide dissolved in a mixture of 6.3 parts of isopropyl alcohol, 0.8 parts of sodium hydroxide and 81 parts of hot water. The coupler solution was added in a thin stream to the cold, stirred diazonium solution. Stirring was continued for two hours while allowing the mixture to warm to 25°C. The mixture was then heated at 50°C. for thirty minutes and then stirred for fifteen hours at 25°C. The pH was adjusted to 6.0 by the addition of a 50 per cent aqueous solution of sodium hydroxide and the reaction mixture then poured into 785 parts of stirred isopropyl alcohol. After stirring the mixture for two hours, the separated yellow solid was collected, washed with fresh isopropyl alcohol, and dried *in vacuo* to obtain the yellow, water-soluble dyestuff of the formula



The visible absorption spectrum of an aqueous solution of this dyestuff, containing 0.02 g. of dye per liter of solution, showed a maximum at 400 millimicrons, $A = 0.975$.

Example 4

Following the procedure described above in Example 1, part A, 16.5 parts of N,N - dimethyl - N - (4 - aminophenyl)carbamyl - methyl - N - 3 - formamidopropylammonium chloride in a solution of 140 parts of water and 36 parts of concentrated hydrochloric acid was diazotized with 3.64 parts of sodium nitrite at 0°C. To the cold diazonium solution thus prepared, there was added in a thin stream, a coupler solution prepared by dissolving 7.2 parts of 2-naphthol in 50 parts of water containing 4.5 parts of 50 per cent aqueous sodium hydroxide solution. The resulting reaction mixture was stirred until all of the diazotized compound was consumed and then was heated to 60°C. To the red mixture there was added 15 parts of sodium chloride and the reaction mixture was allowed to cool to 20°C. The solid was collected and washed with a 10 per cent aqueous sodium chloride solution. The product was dried in a vacuum oven at 75°C. to obtain chiefly the red, highly water-soluble dyestuff having the formula

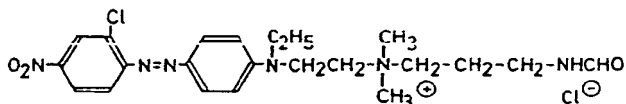


The visible absorption spectrum of an aqueous solution of this dyestuff containing 0.04 g. of dye per liter of solution had a maximum at 380 millimicrons, $A = 1.05$.

Hydrolysis of the formamido moiety in the above-shown product according to the procedure described in Example 1, part B, yields the corresponding $-\text{NH}_2$ substituted compound.

Example 5

A solution of the diazonium compound prepared by treating 8.3 parts of 2-chloro-4-nitroniline in a solution of 50 parts of water and 10.8 parts of concentrated hydrochloric acid with a solution of 3.5 parts of sodium nitrite in 10 parts of water according to the procedure described in Example 1, part A, was added to a solution of 57.7 parts of N,N -dimethyl-N-2-(N' -ethylanilino)ethyl-N-3-formamidopropylammonium chloride in 42 parts of water. The reaction mixture was stirred at 25°C . until the diazonium compound was completely consumed and then 20 parts of sodium chloride was added to the red solution. The reaction was heated to 50°C . and then cooled. The resulting slurry was filtered, and the collected solid washed with a small amount of water and dried *in vacuo* at 75°C . to obtain 24.0 parts of a red, water-soluble dyestuff having the formula

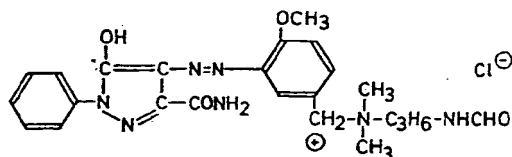


The visible absorption spectrum of an aqueous solution of this dyestuff containing 0.02 g. of dye per liter of solution had a maximum at 492.5 millimicrons, $A = 1.025$.

Hydrolysis of the formamido moiety in the above-shown product according to the procedure described in Example 1, part B, yields the corresponding $-\text{NH}_2$ substituted compound.

Example 6

Proceeding in a manner similar to that described above in Example 1, part A, for diazotizing N,N -dimethyl-N-(3-amino-4-methoxybenzyl)-N-3-formamidopropylammonium chloride and coupling with 3-carbamyl-1-phenyl-2-pyrazolin-5-one, there was obtained the orange-red dyestuff having the formula

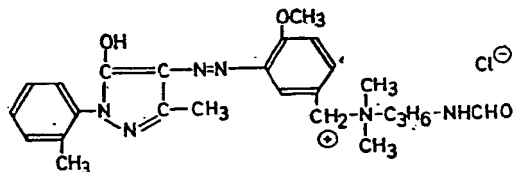


The visible absorption spectrum of an aqueous solution of this dyestuff, containing 0.03 g. of dye per liter of solution, showed a maximum at 450 millimicrons, $A = 1.05$.

Hydrolysis of the formamido moiety in the above-shown product according to the procedure described in Example 1, part B, yields the corresponding $-\text{NH}_2$ substituted compound.

Example 7

Proceeding in a manner similar to that described above in Example 1, part A, for diazotizing N,N -dimethyl-N-(3-amino-4-methoxybenzyl)-N-3-formamidopropylammonium chloride and coupling with 3-methyl-1-(*o*-tolyl)-2-pyrazolin-5-one, there was obtained the orange dyestuff having the formula

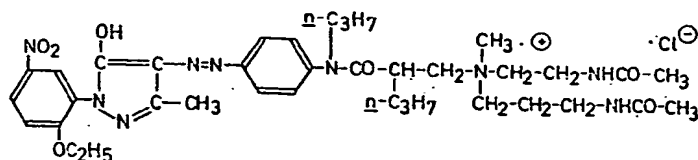


The visible absorption spectrum of an aqueous solution of this dyestuff, containing 0.03 g. of dye per liter of solution, showed a maximum at 412 millimicrons, $A = 1.223$.

Hydrolysis of the formamido moiety in the above-shown product according to the procedure described in Example 1, part B, yielded the corresponding —NH_2 substituted compound, an orange, water-soluble dyestuff. An aqueous solution of this dyestuff, containing 0.03 g. of dye per liter of solution, showed a maximum at 414 millimicrons, $A=1.097$.

Example 8

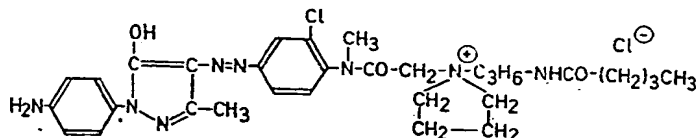
When a procedure similar to that described above in Example 1, part A, is followed for diazotization of N-methyl-N-(2-(N-n-propyl-4-aminophenylcarbonyl)-2-n-propylethyl-N-2-acetamidoethyl-N-3-acetamidopropylammonium chloride and coupling with 3-methyl-1-(2-ethoxy-5-nitrophenyl)-2-pyrazolin-5-one, there is obtained the dyestuff having the formula



Hydrolysis of the two acetamido moieties in the above-shown product according to the procedure described in Example 1, part B, yields the corresponding di(—NH_2) substituted compound.

Example 9

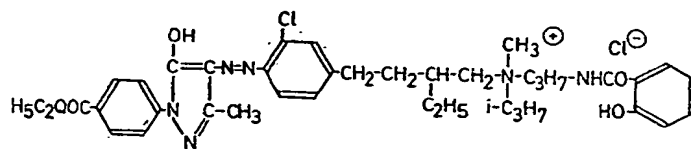
When a procedure similar to that described above in Example 1, part A, is followed for diazotization of N-(4-amino-N-methyl-2-chlorophenyl)methyl-N-3-n-valeramidopropylpyrrolidinium chloride and coupling with 3-methyl-1-(4-aminophenyl)-2-pyrazolin-5-one, there is obtained the dyestuff having the formula



Hydrolysis of the valeramido moiety in the above-shown product according to the procedure described in Example 1, part B, yields the corresponding —NH_2 substituted compound.

Example 10

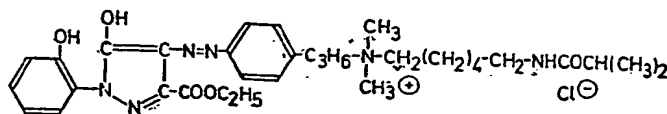
When a procedure similar to that described above in Example 1, part A, is followed for diazotization of N-methyl-N-isopropyl-N-2-ethyl-4-(3-chloro-4-aminophenyl)butyl-N-3-salicylaminoethylammonium chloride and coupling with 3-methyl-1-(4-ethoxycarbonylphenyl)-2-pyrazolin-5-one, there is obtained the dyestuff having the formula



Hydrolysis of the salicylamino moiety in the above-shown product according to the procedure described in Example 1, part B, yields the corresponding —NH_2 substituted compound.

Example 11

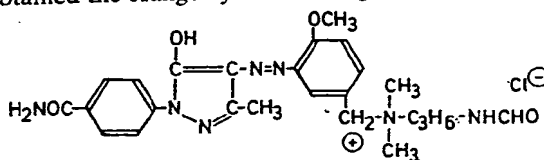
When a procedure similar to that described above in Example 1, part B, is followed for diazotization of N,N-dimethyl-N-3-(4-aminophenyl)propyl-N-6-isobutyramidoethylammonium chloride and coupling with 3-ethoxycarbonyl-1-(2-hydroxyphenyl)-2-pyrazolin-5-one, there is obtained the dyestuff having the formula



Hydrolysis of the iso-butyramido moiety in the above-shown product according to the procedure described in Example 1, part B, yields the corresponding —NH_2 substituted compound.

Example 12

Proceeding in a manner similar to that described above in Example 1, part A, for diazotizing N,N-dimethyl-N-(3-amino-4-methoxybenzyl)-N-3-formamidopropylammonium chloride and coupling with 3-methyl-1-(p-carbamylphenyl)-2-pyrazolin-5-one, there was obtained the orange dyestuff having the formula



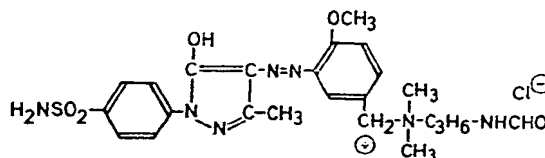
The visible absorption spectrum of an aqueous solution of this dyestuff, containing 0.03 g. of dye per liter of solution, showed a maximum at 412 millimicrons, $A=0.986$.

This dye was found to have a moderate tendency to bleed each in the water bleed and the soap bleed test.

Hydrolysis of the formamido moiety in the above-shown product according to the procedure described in Example 1, part B, yields the corresponding —NH_2 substituted compound.

Example 13

Proceeding in a manner similar to that described above in Example 1, part A, for diazotizing N,N-dimethyl-N-(3-amino-4-methoxybenzyl)-N-3-formamidopropylammonium chloride and coupling with 3-methyl-1-(p-sulfamylphenyl)-2-pyrazolin-5-one, there was obtained the yellow dyestuff having the formula

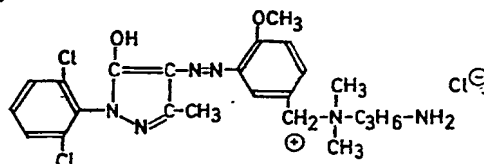


The visible absorption spectrum of an aqueous solution of this dyestuff, containing 0.03 g. per liter of solution, showed a maximum at 415 millimicrons, $A=1.12$.

Hydrolysis of the formamido moiety in the above-shown product according to the procedure described in Example 1, part B, yields the corresponding —NH_2 substituted compound.

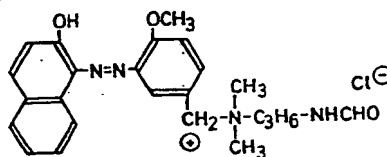
Example 14

Proceeding in a manner similar to that described above in Example 2, N,N-dimethyl-N-(3-amino-4-methoxybenzyl)-N-3-formamidopropylammonium chloride was diazotized and coupled with 3-methyl-1-(2,5-dichlorophenyl)-2-pyrazolin-5-one, and the product hydrolyzed to obtain the orange, water-soluble dyestuff having the formula



Example 15

Proceeding in a manner similar to that described above in Example 1, part A, for diazotizing N,N-dimethyl-N-(3-amino-4-methoxybenzyl)-N-3-formamidopropylammonium chloride and coupling with 2-naphthol, there was obtained the bright red dyestuff having the formula

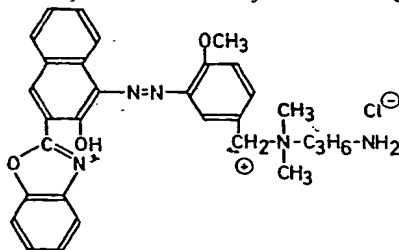


The visible absorption spectrum of an aqueous solution of this dyestuff, containing 0.03 g. of dye per liter of solution, showed a maximum at 494 millimicrons, $A=1.192$.

Hydrolysis of the formamido moiety in the above-shown product according to the procedure described in Example 1, part B, yielded the corresponding $-NH_2$ substituted compound, a red, water-soluble dyestuff. An aqueous solution of this dyestuff, containing 0.04 g. of dye per liter of solution, showed a maximum at 497 millimicrons, $A=0.995$.

Example 16

Proceeding in a manner similar to that described above in Example 3, N,N-dimethyl-N-(3-amino-4-methoxybenzyl)-N-3-formamidopropylammonium chloride was hydrolyzed and the resulting N,N-dimethyl-N-(3-amino-4-methoxybenzyl)-N-3-amino-propylammonium chloride was diazotized and coupled with 3-(benzoxazol-2-yl)-2-naphthol to obtain the red-brown, water-soluble dyestuff having the formula

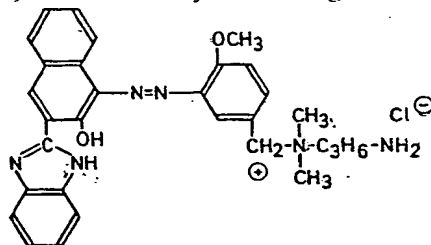


The visible absorption spectrum of an aqueous solution of this dyestuff, containing 0.16 g. of dye per liter of solution, showed two maxima: at 520 millimicrons, $A=0.96$; and at 546 millimicrons, $A=0.94$.

In the bleach test described above, paper dyed with this dyestuff was found to be highly bleachable. The dye was found to bleed slightly and to approximately the same extent each in the water bleed test and the soap bleed test.

Example 17

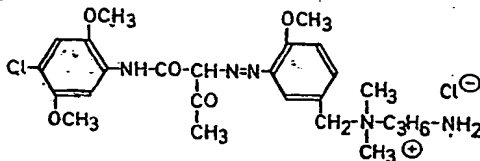
Proceeding in a manner similar to that described above in Example 3, N,N-dimethyl-N-(3-amino-4-methoxybenzyl)-N-3-formamidopropylammonium chloride was hydrolyzed and the resulting N,N-dimethyl-N-(3-amino-4-methoxybenzyl)-N-3-amino-propylammonium chloride was diazotized and coupled with 3-(benzimidazol-2-yl)-2-naphthol to obtain the red, water-soluble dyestuff having the formula



The visible absorption spectrum of an aqueous solution of this dyestuff, containing 0.75 g. of dye per liter of solution, showed a maximum at 520 millimicrons, $A=1.138$.

Example 18

Proceeding in a manner similar to that described above in Example 2, N,N-dimethyl-N-(3-amino-4-methoxybenzyl)-N-3-formamidopropylammonium chloride was diazotized and coupled with 4-chloro-2,5-dimethoxyacetanilide (Naphthol AS 13GH) and the product hydrolyzed to obtain the yellow water-soluble dyestuff having the formula

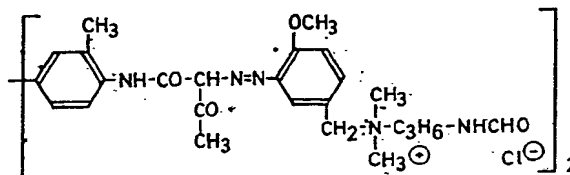


An aqueous solution of this dyestuff, containing 0.10 g. of dye per liter of solution, showed a maximum at 395 millimicrons, $A=1.082$.

This dyestuff was found to bleed slightly in the soap bleed test and the water bleed test.

Example 19

Proceeding in a manner similar to that described above in Example 1, part A, for diazotizing N,N-dimethyl-N-(3-amino-4-methoxybenzyl)-N-3-formamidopropylammonium chloride and coupling with 4,4'-bis-*o*-acetoacetotoluidide (Naphthol AS—G) there was obtained the yellow dyestuff having the formula



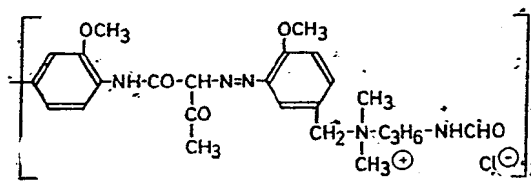
The visible absorption spectrum of an aqueous solution of this dyestuff, containing 0.03 g. of dye per liter of solution, showed a maximum at 399 millimicrons, $A=1.175$.

Hydrolysis of the formamido moieties in the above-shown product according to the procedure described in Example 1, part B, yielded the corresponding di(—NH₂) substituted compound, an orange, highly water-soluble dyestuff. An aqueous solution of this dyestuff, containing 1.0 g. of dye per liter of solution, showed a maximum at 392 millimicrons, $A=1.32$.

This dyestuff was found to bleed slightly in the water bleed test and somewhat less in the soap bleed test.

Example 20

Proceeding in a manner similar to that described above in Example 1, part A, for diazotizing N,N-dimethyl-N-(3-amino-4-methoxybenzyl)-N-3-formamidopropylammonium chloride and coupling with 4,4'-bis-*o*-acetoacetaniside, there was obtained the yellow dyestuff having the formula



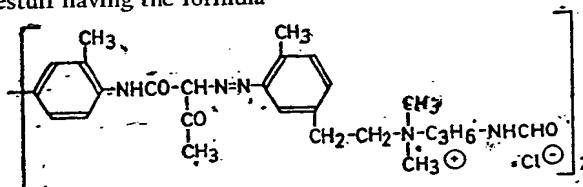
The visible absorption spectrum of an aqueous solution of this dyestuff, containing 0.03 g. of dye per liter of solution, showed a maximum at 406 millimicrons, $A=1.2224$.

Hydrolysis of the formamido moieties in the above-shown product according to the procedure described in Example 1, part B, yielded the corresponding di(—NH₂) substituted compound, an orange, highly water-soluble dyestuff. An aqueous solution of this dyestuff, containing 0.04 g. of dye per liter of solution, showed a maximum at 386 millimicrons, $A=0.92$.

In the bleach test described above, paper dyed with this dyestuff was found to be highly bleachable. The dye was found to bleed slightly in the soap bleed test but substantially less in the water bleed test.

Example 21

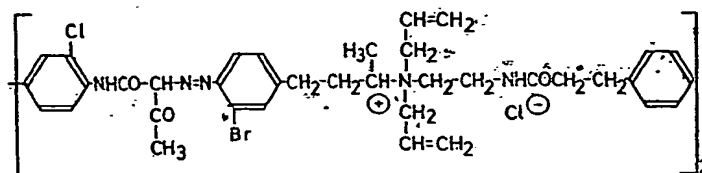
When a procedure similar to that described above in Example 1, part A, is followed for diazotization of N,N-dimethyl-N-2-(3-amino-4-methylphenyl)ethyl-N-3-formamidopropylammonium chloride and coupling with Naphthol AS—G, there is obtained the dyestuff having the formula



Hydrolysis of the formamido moieties in the above-shown product according to the procedure described in Example 1, part B, yields the corresponding di($-\text{NH}_2$) substituted compound.

Example 22

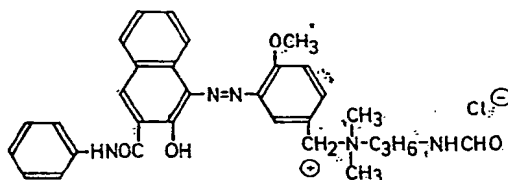
When a procedure similar to that described above in Example 1, part A, is followed for diazotization of *N,N*-diallyl-*N*-1-methyl-3-(4-amino-3-bromophenyl)-propyl-*N*-2-phenylpropionamidoethylammonium chloride and coupling with 2',2''-dichloro-4',4'''-biacetoacetanilide, there is obtained the dyestuff having the formula



Hydrolysis of the phenylpropionamido moieties in the above-shown product according to the procedure described in Example 1, part B, yields the corresponding di($-\text{NH}_2$) substituted compound.

Example 23

Proceeding in a manner similar to that described above in Example 1, part A, for diazotizing *N,N*-dimethyl-*N*-(3-amino-4-methoxybenzyl)-*N*-3-formamidopropylammonium chloride and coupling with 2-hydroxy-3-naphthanilide (Naphthol AS), there was obtained the orange-red dyestuff having the formula

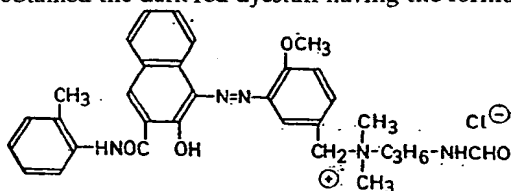


The visible absorption spectrum of an aqueous solution of this dyestuff, containing 0.04 g. of dye per liter of solution, showed a maximum at 514 millimicrons, $A=0.838$.

Hydrolysis of the formamido moiety in the above-shown product according to the procedure described in Example 1, part B, yielded the corresponding $-\text{NH}_2$ substituted compound, a red, water-soluble dyestuff. An aqueous solution of this dyestuff, containing 0.06 g. of dye per liter of solution, showed a maximum at 514 millimicrons, $A=1.223$.

Example 24

Proceeding in a manner similar to that described above in Example 1, part A, for diazotizing *N,N*-dimethyl-*N*-(3-amino-4-methoxybenzyl)-*N*-3-formamidopropylammonium chloride and coupling with 2-hydroxy-3-naphtho-*o*-toluidide (Naphthol AS-D), there was obtained the dark red dyestuff having the formula

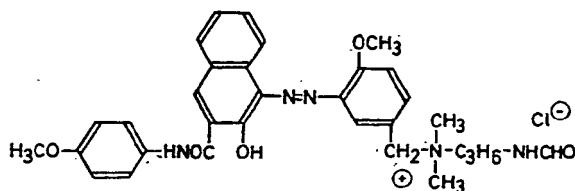


The visible absorption spectrum of an aqueous solution of this dyestuff, containing 0.06 g. of dye per liter of solution, showed a maximum at 518 millimicrons, $A=1.285$.

Hydrolysis of the formamido moiety in the above-shown product according to the procedure described in Example 1, part B, yielded the corresponding $-\text{NH}_2$ substituted compound, a red, water-soluble dyestuff. An aqueous solution of this dyestuff, containing 0.10 g. of dye per liter of solution, showed a maximum at 520 millimicrons, $A=0.995$.

Example 25

Proceeding in a manner similar to that described above in Example 1, part A, for diazotizing N,N-dimethyl-N-(3-amino-4-methoxybenzyl)-N-3-formamidopropylammonium chloride and coupling with 2-hydroxy-3-naphth-*p*-anisidine (Naphthol AS—RL), there was obtained the red, water-soluble dyestuff having the formula

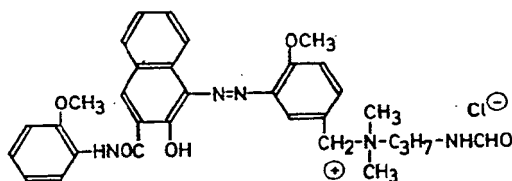


The visible absorption spectrum of an aqueous solution of this dyestuff, containing 0.06 g. of dye per liter of solution, showed a maximum at 515 millimicrons, $A=1.14$.

Hydrolysis of the formamido moiety in the above-shown product according to the procedure described in Example 1, part B, yielded the corresponding $-NH_2$ substituted compound, a red, water-soluble dyestuff. An aqueous solution of this dyestuff, containing 0.05 g. of dye per liter of solution, showed a maximum at 517 millimicrons, $A=0.90$.

Example 26

Proceeding in a manner similar to that described above in Example 1, part A, for diazotizing N,N-dimethyl-N-(3-amino-4-methoxybenzyl)-N-3-formamidopropylammonium chloride and coupling with 2-hydroxy-3-naphth-*o*-anisidine (Naphthol AS—OL), there was obtained the dark red, water-soluble dyestuff having the formula

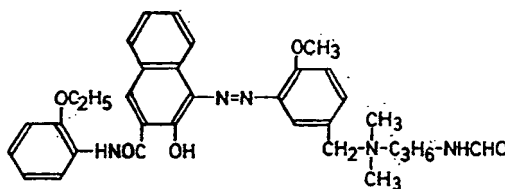


The visible absorption spectrum of an aqueous solution of this dyestuff, containing 0.04 g. of dye per liter of solution, showed a maximum at 514 millimicrons, $A=0.995$.

Hydrolysis of the formamido moiety in the above-shown product according to the procedure described in Example 1, part B, yielded the corresponding $-NH_2$ substituted compound, a red, water-soluble dyestuff. An aqueous solution of this dyestuff, containing 0.04 g. of dye per liter of solution, showed a maximum at 517 millimicrons, $A=0.895$.

Example 27

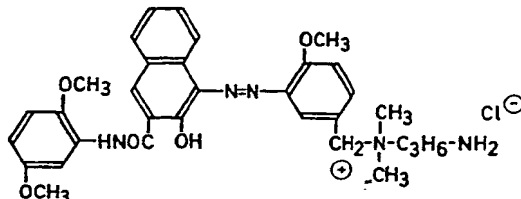
Proceeding in a manner similar to that described above in Example 1, part A, for diazotizing N,N-dimethyl-N-(3-amino-4-methoxybenzyl)-N-3-formamidopropylammonium chloride and coupling with 2-hydroxy-3-naphtho-*o*-phenetide (Naphthol AS—PH), there was obtained the red, water-soluble dyestuff having the formula



The visible absorption spectrum of an aqueous solution of this dyestuff, containing 0.05 g. of dye per liter of solution, showed a maximum at 512.5 millimicrons, $A=1.1$.

Example 31

Proceeding in a manner similar to that described above in Example 3, N,N-dimethyl-N-(3-amino-4-methoxybenzyl)-N-3-formamidopropylammonium chloride was hydrolyzed and the resulting N,N-dimethyl-N-(3-amino-4-methoxybenzyl)-N-3-aminopropylammonium chloride was diazotized and coupled with 2-hydroxy-2',5'-dimethoxy-3-naphthanilide (Naphthol AS—BG), to obtain the red, water-soluble dyestuff having the formula

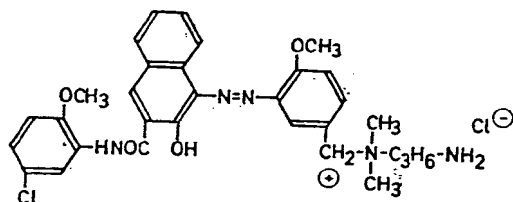


The visible absorption spectrum of an aqueous solution of this dyestuff, containing 0.04 g. of dye per liter of solution, showed two maxima: at 517.5 millimicrons, $A = 1.25$; and at 543 millimicrons, $A = 1.23$.

In the bleach test described above, paper dyed with this dyestuff was found to be readily bleachable. The dye was found to bleed slightly and to approximately the same extent each in the water bleed test and the soap bleed test.

Example 32

Proceeding in a manner similar to that described above in Example 3, N,N-dimethyl-N-(3-amino-3-methoxybenzyl)-N-3-formamidopropylammonium chloride was hydrolyzed and the resulting N,N-dimethyl-N-(3-amino-4-methoxybenzyl)-N-3-aminopropylammonium chloride was diazotized and coupled with 5'-chloro-2-hydroxy-2'-methoxy-3-naphthanilide (Naphthol AS—EL) to obtain the red, water-soluble dyestuff having the formula

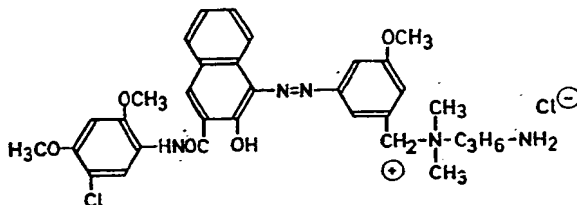


The visible absorption spectrum of an aqueous solution of this dyestuff, containing 0.06 g. of dye per liter of solution, showed two maxima: at 518 millimicrons, $A = 1.07$; and at 545 millimicrons, $A = 1.08$.

In the bleach test described above, paper dyed with this dyestuff was found to be readily bleachable. The dye was found to bleed slightly in the soap bleed test but significantly less in the water bleed test.

Example 33

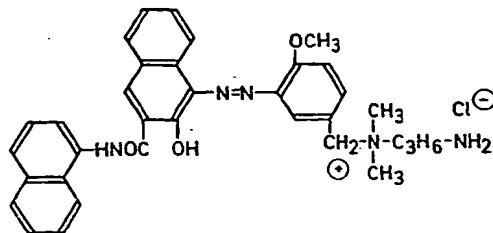
Proceeding in a manner similar to that described above in Example 3, N,N-dimethyl-N-(3-amino-4-methoxybenzyl)-N-3-formamidopropylammonium chloride was hydrolyzed and the resulting N,N-dimethyl-N-(3-amino-4-methoxybenzyl)-N-3-aminopropylammonium chloride was diazotized and coupled with 5'-chloro-2-hydroxy-2',4'-dimethoxy-3-naphthanilide (Naphthol AS—ITR), to obtain the red, water-soluble dyestuff having the formula



The visible absorption spectrum of an aqueous solution of this dyestuff, containing 0.05 g. of dye per liter of solution, showed two maxima: at 519 millimicrons, $A = 0.885$; and at 545 millimicrons, $A = 0.86$.

Example 34

Proceeding in a manner similar to that described above in Example 3, N,N-dimethyl-N-(3-amino-4-methoxybenzyl)-N-3-formamidopropylammonium chloride was hydrolyzed and the resulting N,N-dimethyl-N-(3-amino-4-methoxybenzyl)-N-3-aminopropylammonium chloride was diazotized and coupled with 2-hydroxy-N-1-naphthyl-3-naphthanilide (Naphthol AS—BO), to obtain the red, water-soluble dyestuff having the formula

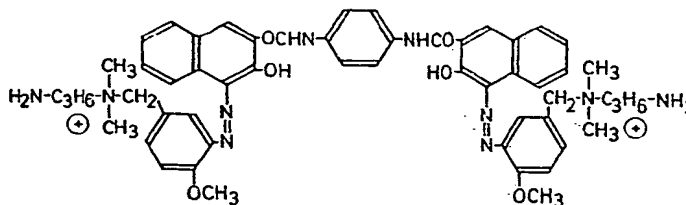


The visible absorption spectrum of an aqueous solution of this dyestuff, containing 0.08 g. of dye per liter of solution, showed two maxima: at 521 millimicrons, $\lambda = 1.478$; and at 547 millimicrons, $\lambda = 434$.

In the bleach test described above, paper dyed with this dyestuff was found to be readily bleachable. The dye was found to bleed slightly in the soap bleed test but significantly less in the water bleed test.

Example 35

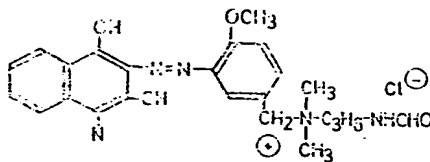
Proceeding in a manner similar to that described above in Example 2, N,N-dimethyl-N-(3-amino-4-methoxybenzyl)-N-3-formamidopropylammonium chloride was diazotized and coupled with N,N'-p-phenylenebis(2-hydroxy-3-naphthamide) and the product hydrolyzed to obtain the bluish-red, water-soluble dyestuff having the formula



An aqueous solution of this dyestuff, containing 0.06 g. of dye per liter of solution, showed a maximum at 512 millimicrons, $\lambda = 1.095$.

Example 36

Proceeding in a manner similar to that described above in Example 1, part A, for diazotizing N,N-dimethyl-N-(3-amino-4-methoxybenzyl)-N-3-formamidopropylammonium chloride and coupling with 2,4-dihydroxyquinoline, there was obtained the yellow, water-soluble dyestuff having the formula

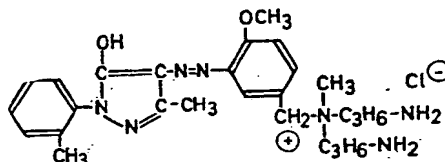


The visible absorption spectrum of an aqueous solution of this dyestuff, containing 0.03 g. of dye per liter of solution, showed a maximum at 442 millimicrons, $\lambda = 1.28$.

Hydrolysis of the formamido moiety in the above-shown product according to the procedure described in Example 1, part B, yields the corresponding $-NH_2$ substituted compound.

Example 37

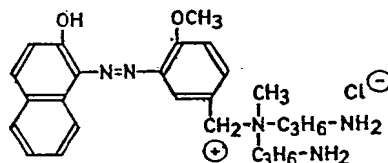
Proceeding in a manner similar to that described above in Example 2, N-methyl-N-(3-amino-4-methoxybenzyl)-N,N-bis(3-formamidopropyl)ammonium chloride was diazotized and coupled with 3-methyl-1-(o-tolyl)-2-pyrazolin-5-one, and the product hydrolyzed to obtain the yellow, water-soluble dyestuff having the formula



An aqueous solution of this dyestuff, containing 0.5 g. of dye per liter of solution, showed a maximum at 415 millimicrons, $A = 1.21$.

Example 38

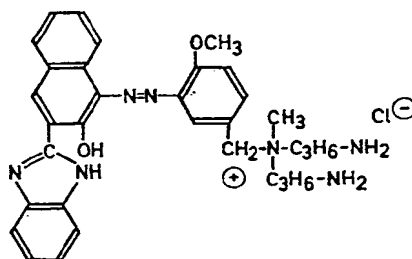
Proceeding in a manner similar to that described above in Example 2, N-methyl-N-(3-amino-4-methoxybenzyl)-N,N-bis(3-formamidopropyl)ammonium chloride was diazotized and coupled with 2-naphthol, and the product hydrolyzed to obtain the red, water-soluble dyestuff having the formula



An aqueous solution of this dyestuff, containing 0.04 g. of dye per liter of solution, showed a maximum at 500 millimicrons, $A = 0.912$.

Example 39

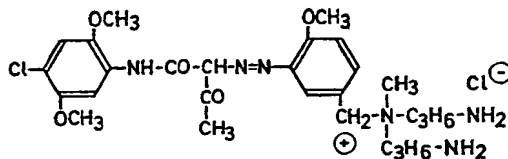
Proceeding in a manner similar to that described above in Example 3, N-methyl-N-(3-amino-4-methoxybenzyl)-N,N-bis(3-formamidopropyl)ammonium chloride was hydrolyzed and the resulting N-methyl-N-(3-amino-4-methoxybenzyl)-N,N-bis(3-aminopropyl)ammonium chloride was diazotized and coupled with 3-(benzimidazol-2-yl)-2-naphthol, to obtain the red, water-soluble dyestuff having the formula



The visible absorption spectrum of an aqueous solution of this dyestuff, containing 1.0 g. of dye per liter of solution, showed a maximum at 526 millimicrons $A = 1.05$.

Example 40

Proceeding in a manner similar to that described above in Example 2, N-methyl-N-(3-amino-4-methoxybenzyl)-N,N-bis(3-formamidopropyl)ammonium chloride was diazotized and coupled with 4-chloro-2,5-dimethoxyacetoacetanilide (Naphthol AS13GH), and the product hydrolyzed to obtain the yellow, water-soluble dyestuff having the formula

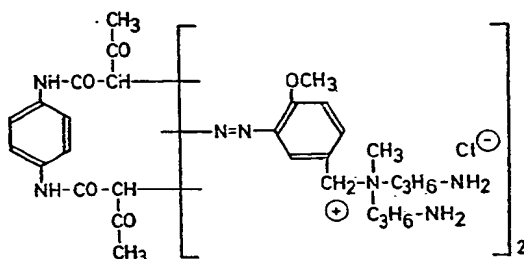


An aqueous solution of this dyestuff, containing 0.25 g. of dye per liter of solution, showed a maximum at 395.3 millimicrons, $A=0.954$.

In the bleach test described above, paper dyed with this dyestuff was found to be readily bleachable. The dye was found to bleed slightly and to approximately the same extent each in the water bleed test and the soap bleed test.

Example 41

Proceeding in a manner similar to that described above in Example 2, N-methyl-N-(3-amino-4-methoxybenzyl)-N,N-bis(3-formamidopropyl)ammonium chloride was diazotized and coupled with N,N-diacetoacet-*p*-phenylenediamine and the product hydrolyzed to obtain the yellow, water-soluble dyestuff having the formula

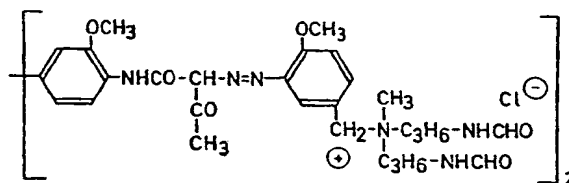


An aqueous solution of this dyestuff, containing 0.2 g. of dye per liter of solution, showed a maximum at 394 millimicrons, $A=0.9$.

In the bleach test described above, paper dyed with this dyestuff was found to be highly bleachable. The dye was found to bleed slightly in the water bleed test with substantially less bleeding in the soap bleed test.

Example 42

Proceeding in a manner similar to that described above in Example 1, part A, for diazotizing N-methyl-N-(3-amino-4-methoxybenzyl)-N,N-bis(3-formamidopropyl) ammonium chloride and coupling with 4,4'-bis-*o*-acetoacetanilide, there was obtained the orange, water-soluble dyestuff having the formula



The visible absorption spectrum of an aqueous solution of this dyestuff, containing 0.03 g. of dye per liter of solution, showed a maximum at 412 millimicrons, $A=1.255$.

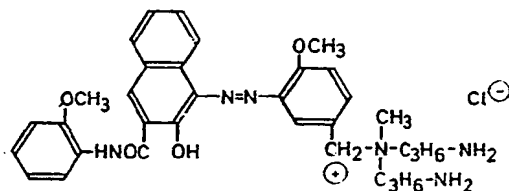
Hydrolysis of the four formamido moieties in the above-shown product according to the procedure described in Example 1, part B, yielded the corresponding tetra- $(-NH_2)$ substituted compound, a yellow, highly water-soluble dyestuff. An aqueous solution of this dyestuff, containing 0.75 g. of dye per liter of solution, showed a maximum at 400 millimicrons, $A=0.975$.

In the bleach test described above, paper dyed with this dyestuff was found to be readily bleachable. The dye was found to bleed slightly in the soap bleed test with substantially less bleeding in the water bleed test.

Example 43

Proceeding in a manner similar to that described above in Example 2, N-methyl-N-(3-amino-4-methoxybenzyl)-N,N-bis(3-formamidopropyl)ammonium chloride was diazotized and coupled with 2-hydroxy-3-naphth-*o*-anisidide (Naphthol AS-OL),

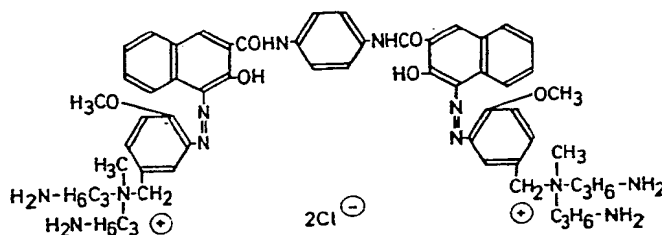
and the product hydrolyzed to obtain the red, water-soluble dyestuff having the formula



An aqueous solution of this dyestuff, containing 0.4 g. of dye per liter of solution, showed a maximum at 517 millimicrons, $A = 0.997$.

Example 44

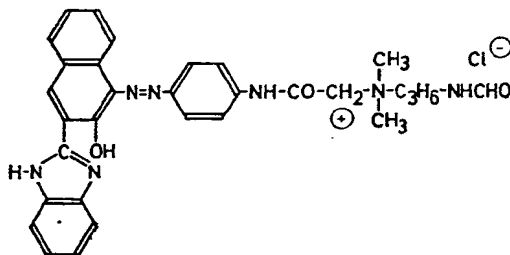
Proceeding in a manner similar to that described above in Example 2, N-methyl-N-(3-amino-4-methoxybenzyl)-N,N-bis(3-formamidopropyl)ammonium chloride was diazotized and coupled with N,N'-p-phenylenebis(2-hydroxy-3-naphthamide), and the product hydrolyzed to obtain the dyestuff having the formula



An aqueous solution of this dyestuff, containing 0.06 g. of dye per liter of solution, showed a maximum at 517 millimicrons, $A = 0.78$.

Example 45

Proceeding in a manner similar to that described above in Example 1, part A, for diazotizing N,N-dimethyl-N-(4-aminophenyl)carbonylmethyl-N-3-formamidopropylammonium chloride and coupling with 3-(benzimidazol-2-yl)-2-naphthol, there was obtained the red, water-soluble dyestuff having the formula

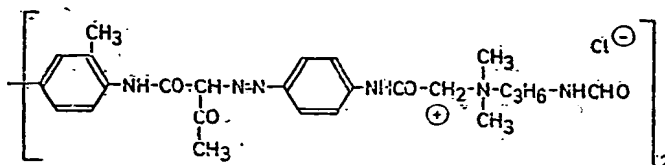


The visible absorption spectrum of an aqueous solution of this dyestuff, containing 1.0 g. of dye per liter of solution, showed a maximum at 524 millimicrons, $A = 1.36$.

Hydrolysis of the formamido moiety in the above-shown product according to a procedure described in Example 24, part B, yields the corresponding $-NH_2$ substituted compound.

Example 46

Proceeding in a manner similar to that described above in Example 1, part A, for diazotizing N,N-dimethyl-N-(4-aminophenyl)carbonylmethyl-N-3-formamido-propylammonium chloride and coupling with 4,4'-bis-*o*-acetoacetotoluidide (Naphthol AS-G), there was obtained the yellow-brown, water-soluble dyestuff having the formula

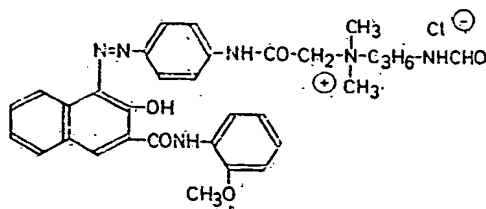


The visible absorption spectrum of an aqueous solution of this dyestuff, containing 0.02 g. of dye per liter of solution, showed a maximum at 395 millimicrons, $A=0.855$.

Hydrolysis of the formamido moieties in the above-shown product according to the procedure described in Example 1, part B, yields the corresponding di($-NH_2$) substituted compound.

Example 47

Proceeding in a manner similar to that described above in Example 1, part A, for diazotizing N,N-dimethyl-N-(4-aminophenyl)carbonylmethyl-N-3-formamido-propylammonium chloride and coupling with 2-hydroxy-3-naphth-*o*-aniside (Naphthol AS-OL), there was obtained the red-brown, water-soluble dyestuff having the formula

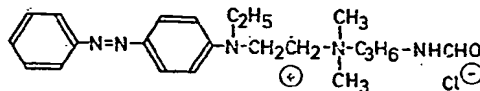


The visible absorption spectrum of an aqueous solution of this dyestuff, containing 0.04 g. of dye per liter of solution, showed a maximum at 516 millimicrons, $A=1.095$.

Hydrolysis of the formamido moiety in the above-shown product according to the procedure described in Example 1, part B, yields the corresponding $-NH_2$ substituted compound.

Example 48

Proceeding in a manner similar to that described above in Example 5, for diazotizing aniline and coupling with N,N-dimethyl-N-2-(N'-ethylanilino)ethyl-N-3-formamidopropylammonium chloride, there was obtained the yellow, water-soluble dyestuff having the formula



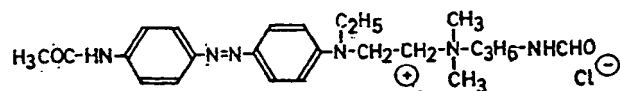
The visible absorption spectrum of an aqueous solution of this dyestuff, containing 0.156 g. of dye per liter of solution, showed a maximum at 410 millimicrons, $A=0.92$.

Hydrolysis of the formamido moiety in the above-shown product according to the procedure described in Example 1, part B, yields the corresponding $-NH_2$ substituted compound.

Example 49

Proceeding in a manner similar to that described above in Example 5, for diazotizing *p*-aminoacetanilide and coupling with N,N-dimethyl-N-2-(N'-ethyl-

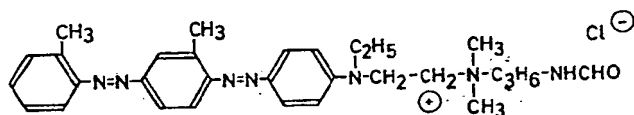
anilino)ethyl-N-3-formamidopropylammonium chloride, there was obtained the yellow, water-soluble dyestuff having the formula



- 5 The visible absorption spectrum of an aqueous solution of this dyestuff, containing 0.375 g. of dye liter of solution, showed a maximum at 424 millimicrons, $A = 0.985$. Hydrolysis of the formamido moiety in the above-shown product according to the procedure described in Example 1, part B, yields the corresponding —NH_2 substituted compound.

Example 50

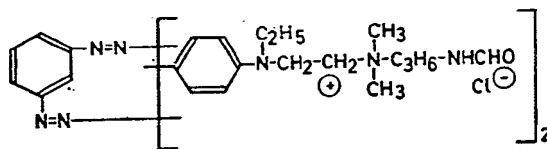
- 10 Proceeding in a manner similar to that described above in Example 5, for diazotizing 4-*o*-tolylazo-*o*-toluidine and coupling with N,N-dimethyl-N-2-(N'-ethylanilino)ethyl-N-3-formamidopropylammonium chloride, there was obtained the brown, water-soluble dyestuff having the formula



- 15 The visible absorption spectrum of an aqueous solution of this dyestuff, containing 0.625 g. of dye per liter of solution, showed a maximum at 455 millimicrons, $A = 1.085$. Hydrolysis of the formamido moiety in the above-shown product according to the procedure described in Example 1, part B, yields the corresponding —NH_2 substituted compound.

Example 51

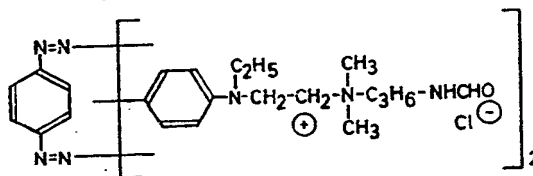
- 20 Proceeding in a manner similar to that described above in Example 5 for diazotizing *m*-phenylene diamine and coupling with N,N-dimethyl-N-2-(N'-ethylanilino)ethyl-N-3-formamidopropylammonium chloride, there was obtained the yellow-brown, water-soluble dyestuff having the formula



- 25 The visible absorption spectrum of an aqueous solution of this dyestuff, containing 0.25 g. of dye per liter of solution, showed a maximum at 427.5 millimicrons, $A = 1.21$. Hydrolysis of the formamido moieties in the above-shown product according to the procedure described in Example 1, part B, yields the corresponding di(—NH_2) substituted compound.

Example 52

- 30 Proceeding in a manner similar to that described above in Example 5, for diazotizing 3,3'-dichlorobenzidine and coupling with N,N-dimethyl-N-2-(N'-ethylanilino)ethyl-N-3-formamidopropylammonium chloride, there was obtained the brown, water-soluble dyestuff having the formula

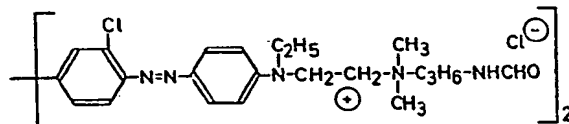


The visible absorption spectrum of an aqueous solution of this dyestuff, containing 0.8 g. of dye per liter of solution, showed a maximum at 437.5 millimicrons, $A = 1.62$.

Hydrolysis of the formamido moieties in the above-shown product according to the procedure described in Example 1, part B, yields the corresponding di-(—NH_2) substituted compound.

Example 53

Proceeding in a manner similar to that described above in Example 5, for diazotizing 3,3' - dichlorobenzidine and coupling with N,N - dimethyl - N - 2 - (N' - ethylanilino)ethyl - N - 3 - formamidopropylammonium chloride, there was obtained the orange-red, water-soluble dyestuff having the formula

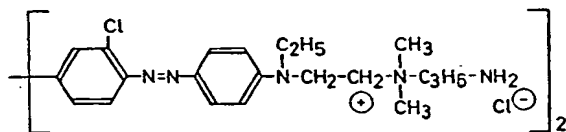


The visible absorption spectrum of an aqueous solution of this dyestuff, containing 0.15 g. of dye per liter of solution, showed a maximum at 486 millimicrons, $A = 1.19$.

Hydrolysis of the formamido moieties in the above-shown product according to the procedure described in Example 1, yields the corresponding di-(—NH_2) substituted compound.

Example 54

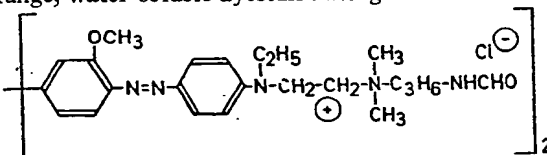
Proceeding in a manner similar to that described above in Example 1, part B, N,N - dimethyl - N - 2 - (N' - ethylanilino)ethyl - N - 3 - formamidopropylammonium chloride was hydrolyzed and the resulting N,N - dimethyl - N - 2 - (N' - ethylanilino)ethyl - N - 3 - aminopropylammonium chloride was coupled with diazotized 3,3' - dichlorobenzidine to obtain the orange-red, water-soluble dyestuff having the formula



The visible absorption spectrum of an aqueous solution of this dyestuff, containing 0.125 g. of dye per liter of solution, showed a maximum at 487 millimicrons, $A = 1.245$.

Example 55

Proceeding in a manner similar to that described above in Example 5, for diazotizing 3,3' - dimethoxybenzidine and coupling with N,N - dimethyl - N - 2 - (N' - ethylanilino)ethyl - N - 3 - formamidopropylammonium chloride, there was obtained the red-orange, water-soluble dyestuff having the formula

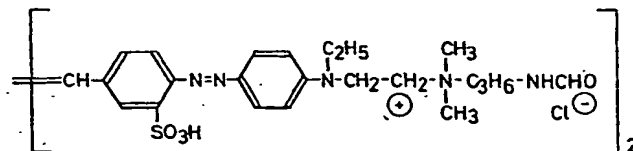


The visible absorption spectrum of an aqueous solution of this dyestuff, containing 0.1875 g. of dye per liter of solution, showed a maximum at 471 millimicrons, $A = 1.03$.

Hydrolysis of the formamido moieties in the above-shown product according to the procedure described in Example 1, part B, yields the corresponding di-(—NH_2) substituted compound.

Example 56

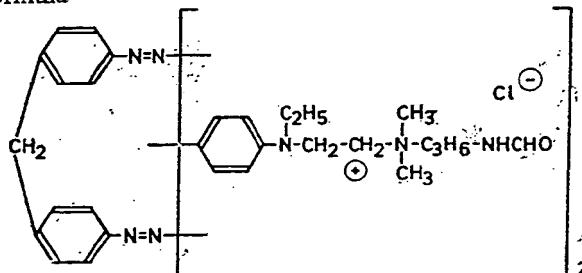
Proceeding in a manner similar to that described above in Example 5, for diazotizing 4,4' - diaminostilbene - 2,2' - disulfonic acid and coupling with N,N - dimethyl - N - 2 - (N' - ethylanilino) - ethyl - N - 3 - formamidopropylammonium chloride, there was obtained the red, water-soluble dyestuff having the formula



Hydrolysis of the formamido moieties in the above-shown product according to the procedure described in Example 1, part B, yields the corresponding di(—NH_2) substituted compound.

Example 57

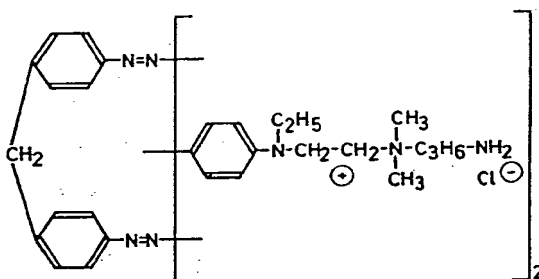
Proceeding in a manner similar to that described above in Example 5, diazotizing 4,4'-methylenedianiline and coupling with N,N-dimethyl-N-2-(N'-ethyl-anilino)ethyl-N-3-formamidopropylammonium chloride yielded the yellow dyestuff having the formula



The visible absorption spectrum of an aqueous solution of this dyestuff, containing 0.1563 g. of dye per liter of solution, showed a maximum at 418 millimicrons, $A = 1.296$.

Example 58

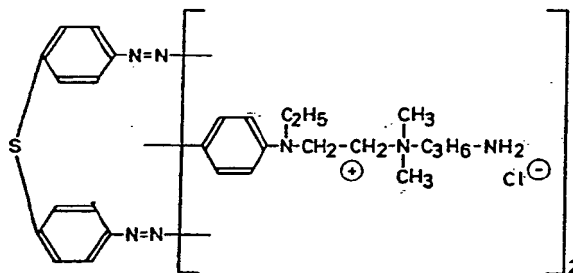
Proceeding in a manner similar to that described above in Example 3, N,N-dimethyl-N-2-(N'-ethyl-anilino)ethyl-N-3-formamidopropylammonium chloride was hydrolyzed and the resulting N,N-dimethyl-N-2-(N'-ethyl-anilino)-ethyl-N-3-aminopropylammonium chloride was coupled with diazotized 4,4'-methylenedianiline to obtain the orange-yellow, water-soluble dyestuff having the formula



The visible absorption spectrum of an aqueous solution of this dyestuff, containing 0.1875 g. of dye per liter of solution, showed a maximum at 420 millimicrons, $A = 1.393$.

Example 59

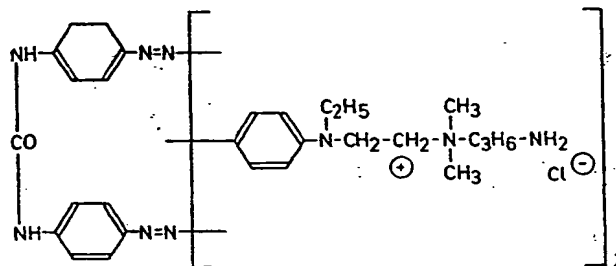
Proceeding in a manner similar to that described above in Example 3, N,N-dimethyl-N-2-(N'-ethyl-anilino)ethyl-N-3-formamidopropylammonium chloride was hydrolyzed and the resulting N,N-dimethyl-N-2-(N'-ethyl-anilino)-ethyl-N-3-aminopropylammonium chloride was coupled with diazotized 4,4'-diaminodiphenylsulfide to obtain the orange-yellow, water-soluble dyestuff having the formula



The visible absorption spectrum of an aqueous solution of this dyestuff, containing 0.102 g. of dye per liter of solution, showed a maximum at 435 millimicrons, $A = 1.015$.

Example 60

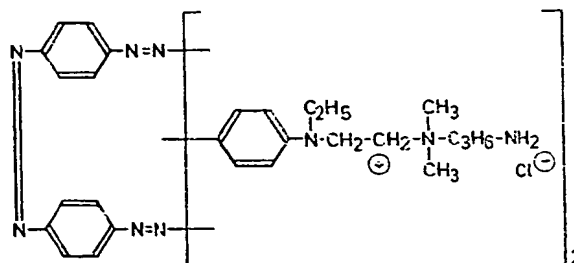
Proceeding in a manner similar to that described above in Example 3, N,N-dimethyl - N - 2 - (N' - ethylanilino)ethyl - N - 3 - formamidopropylammonium chloride was hydrolyzed and the resulting N,N - dimethyl - N - 2 - (N' - ethylanilino)ethyl - N - 3 - aminopropylammonium chloride was coupled with diazotized 4,4'-diaminodiphenylurea to obtain the dark-brown, water-soluble dyestuff having the formula



The visible absorption spectrum of an aqueous solution of this dyestuff, containing 0.03 g. of dye per liter of solution, showed a maximum at 423 millimicrons, $A = 1.37$.

Example 61

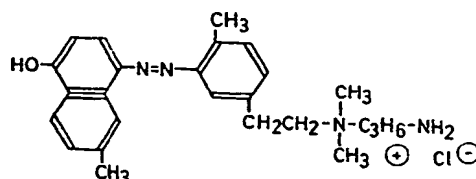
Proceeding in a manner similar to that described above in Example 3, N,N-dimethyl - N - 2 - (N' - ethylanilino)ethyl - N - 3 - formamidopropylammonium chloride was hydrolyzed and the resulting N,N - dimethyl - N - 2 - (N' - ethylanilino)ethyl - N - 3 - aminopropylammonium chloride was coupled with diazotized 4,4' - diamino - azobenzene to obtain the brown, water-soluble dyestuff having the formula



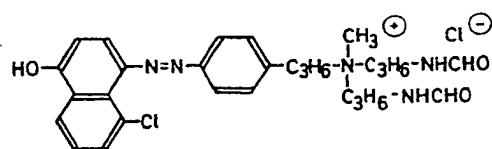
The visible absorption spectrum of an aqueous solution of this dyestuff, containing 0.25 g. of dye per liter of solution, showed a maximum at 494 millimicrons, $A = 1.05$.

In addition to the dyestuffs shown in the foregoing Examples, the following aromatic azo quaternary ammonium dyestuffs are obtained by following the procedures of the instant invention for the coupling of the novel quaternary ammonium intermediates either of Formula III with a coupling component herein defined by Z or of the Formula IV with a diazonium salt obtained by diazotization of an amine herein defined by the formula T-(NH₂)_n.

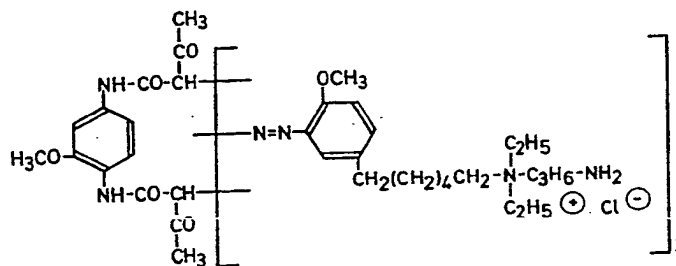
Example 62



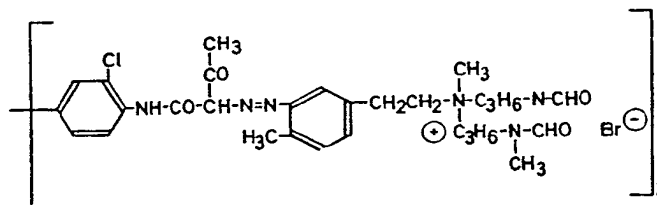
Example 63



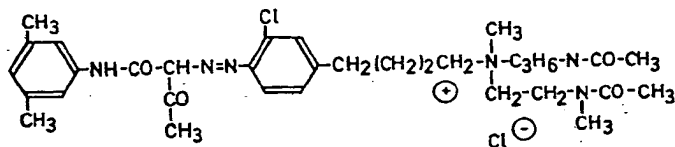
Example 64



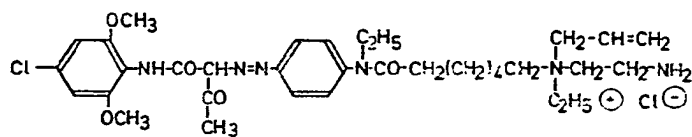
Example 65



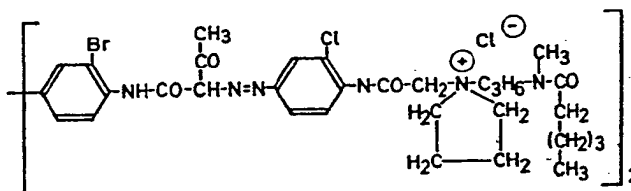
Example 66



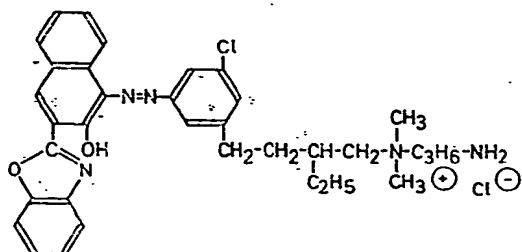
Example 67



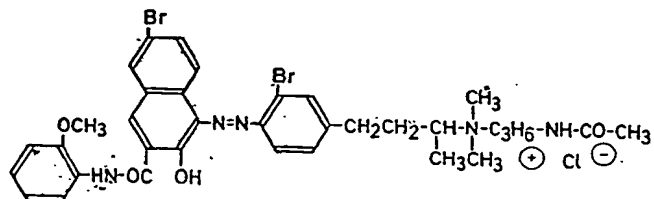
Example 68



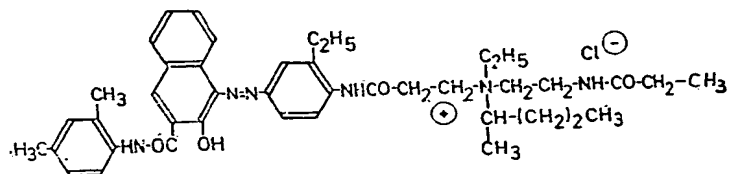
Example 69



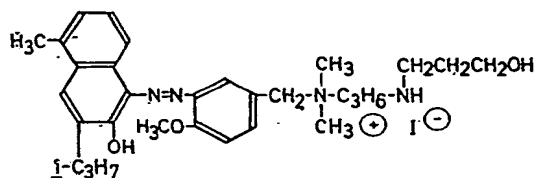
Example 70



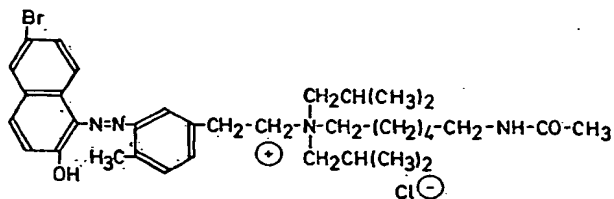
Example 71



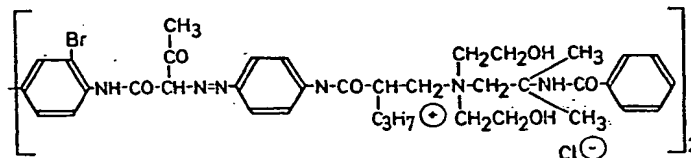
Example 72



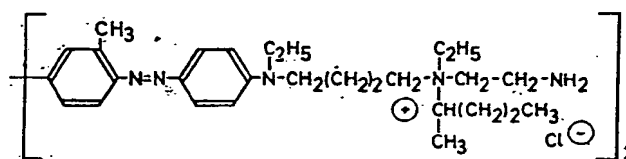
Example 73



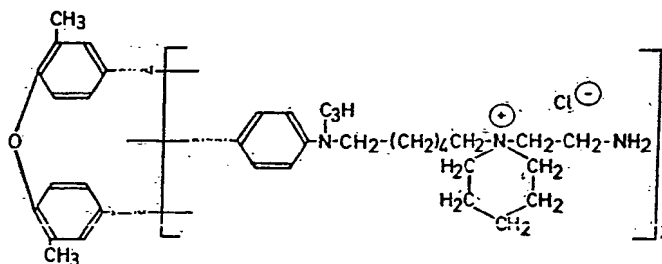
Example 74



Example 75

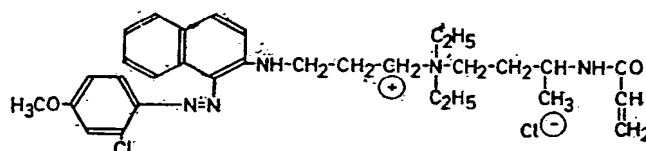


Example 76



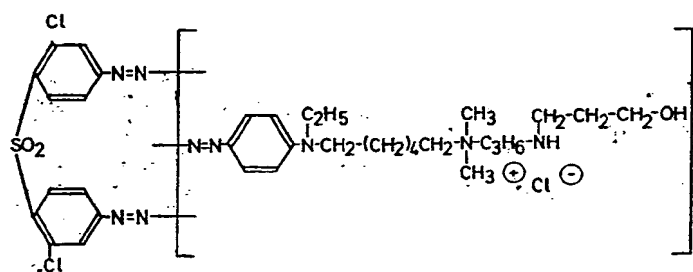
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Example 77

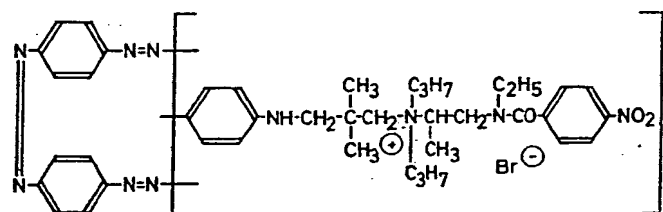


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Example 78



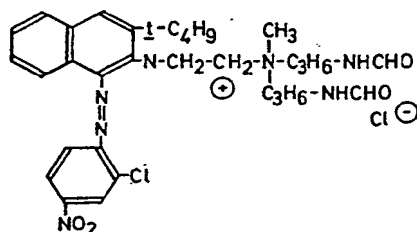
Example 79



10

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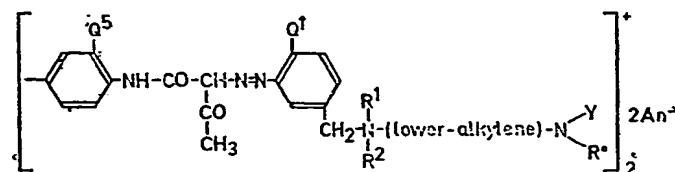
Example 80



WHAT WE CLAIM IS:—

1. A water-soluble quaternary ammonium dyestuff of the Formula I as herein defined.

2. A water-soluble quaternary ammonium dyestuff according to claim 1, wherein c is two, (lower-alkylene)¹ is methylene, said dyestuff having the formula



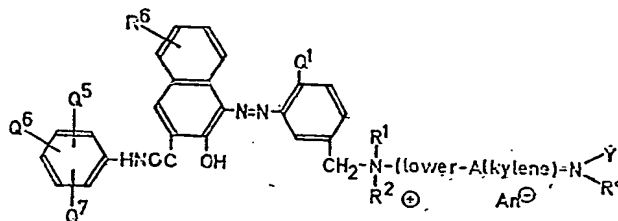
in which Q¹, Q⁵, R⁰, R¹, R², Y and An have the same respective meanings indicated in claim 1.

3. A water-soluble quaternary ammonium dyestuff according to claim 2, wherein (lower-alkylene) is 1,3-propylene; R⁰ is hydrogen; R¹ and R² are each methyl; Q¹ is methoxy; and Q⁵ is methyl or methoxy.

4. A water-soluble quaternary ammonium dyestuff according to claim 3, wherein Y is hydrogen; and Q⁵ is methyl.

5. A water-soluble quaternary ammonium dyestuff according to claim 3, wherein Y is hydrogen and Q⁵ is methoxy.

6. A water-soluble quaternary ammonium dyestuff according to claim 1, wherein c is one, (lower-alkylene)¹ is methylene, said dyestuff having the formula



in which Q¹, Q⁵, Q⁶, Q⁷, R⁰, R¹, R², R⁶, Y and An have the same respective meanings indicated in claim 1.

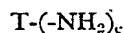
7. A water-soluble quaternary ammonium dyestuff according to claim 6, wherein (lower-alkylene) is 1,3-propylene; Q¹ is methoxy; Q⁵ is 3-nitro; R¹ and R² are each methyl; and Q⁶, Q⁷, R⁰ and R⁶ are each hydrogen.

8. A water-soluble quaternary ammonium dyestuff according to claim 6, wherein (lower-alkylene) is 1,3-propylene; Q¹ is methoxy; Q⁵ is 2-methoxy; Q⁷ is 5-methoxy; R¹ and R² are each methyl; and Q⁶, R⁰ and R⁶ are each hydrogen.

9. A dyestuff of the Formula II as herein defined.

10. A process for preparing the water-soluble quaternary ammonium dyestuff according to claim 1, which comprises diazotizing an amine of the Formula III (as herein defined) and coupling approximately c molecular proportions of the diazonium salt with one molecular proportion of a coupling component, Z, wherein c, R⁰, R¹, R², An, Y, Y¹ and Z each have the same respective meanings indicated in claim 1, and, if desired, hydrolyzing with dilute aqueous mineral acid a compound obtained wherein Y is lower-alkanoyl, lower-alkenoyl, benzoyl or phenyl-lower-alkanoyl to obtain the corresponding compound wherein Y is hydrogen.

11. A process for preparing the water-soluble quaternary ammonium dyestuff according to claim 9, which comprises coupling approximately c molecular proportions of a compound of the Formula IV (as herein defined) with one molecular proportion of the diazonium salt obtained by diazotization of an amine having the formula



wherein c, T, R⁰, R¹, R², An, Y and Y² each have the same respective meanings indicated in claim 9, and, if desired, hydrolyzing with dilute aqueous mineral acid a compound obtained wherein Y is lower-alkanoyl, lower-alkenoyl, benzoyl or phenyl-lower-alkanoyl to obtain the corresponding compound wherein Y is hydrogen.

12. A process for preparing a dyestuff according to claim 1 or 9 substantially as herein described with reference to any of the Examples.
13. A dyestuff prepared by the process according to any one of claims 10 to 12.
14. A dyestuff according to claim 1 or 9 substantially as herein described.

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Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1972.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.